CHAPTER 18

Chemical Equilibrium

What You'll Learn

- You will discover that many reactions and processes reach a state of equilibrium.
- You will use Le Châtelier's principle to explain how various factors affect chemical equilibria.
- You will calculate equilibrium concentrations of reactants and products using the equilibrium constant expression.
- You will determine the solubilities of sparingly soluble ionic compounds.

Why It's Important

The concentrations of substances called acids and bases in your blood are crucial to your health. These substances continuously enter and leave your bloodstream, but the chemical equilibria among them maintain the balance needed for good health.

CLICK HERE

CHEMISTRY Online

Visit the Chemistry Web site at **science.glencoe.com** to find links about chemical equilibrium.

One of the most important of ammonia's many uses is as a fertilizer.

DISCOVERY LAB

Materials

100-mL beaker
graduated cylinder
glass tubes, equal diameter, open at both ends (2)

What's equal about equilibrium?

Does equilibrium mean that the amounts of reactants and products are equal?

Safety Precautions

Always wear safety goggles and a lab apron.

Procedure

1. Measure 20 mL of water in a graduated cylinder and pour it into a 100-mL beaker. Fill the graduated cylinder to the 20-mL mark. Place a glass tube in the graduated cylinder and another glass tube in the beaker. The tubes should reach the bottoms of the containers.
2. Cover the open ends of both glass tubes with your index fingers. Simultaneously, transfer the water from the cylinder to the beaker, and from the beaker to the cylinder.
3. Repeat the transfer process about 25 times. Record your observations.

Analysis

How can you explain your observations during the transfer process? What does this tell you about the concept of equilibrium?

Section 18.1

Equilibrium: A State of Dynamic Balance

Objectives

- **Recognize** the characteristics of chemical equilibrium.
- **Write** equilibrium expressions for systems that are at equilibrium.
- **Calculate** equilibrium constants from concentration data.

Vocabulary

reversible reaction
chemical equilibrium
law of chemical equilibrium
equilibrium constant
homogeneous equilibrium
heterogeneous equilibrium

When you get off a whirling amusement park ride, you probably pause a minute to "get your equilibrium." If so, you are talking about getting your balance back after the ride exerted rapidly changing forces on you. But soon you are balanced steadily on your feet once more. Often, chemical reactions also reach a point of balance or equilibrium. The **DISCOVERY LAB** is an analogy for chemical equilibrium. You found that a point of balance was reached in the transfer of water from the beaker to the graduated cylinder and from the graduated cylinder to the beaker.

What is equilibrium?

Consider the reaction for the formation of ammonia from nitrogen and hydrogen that you learned about in Chapter 16.

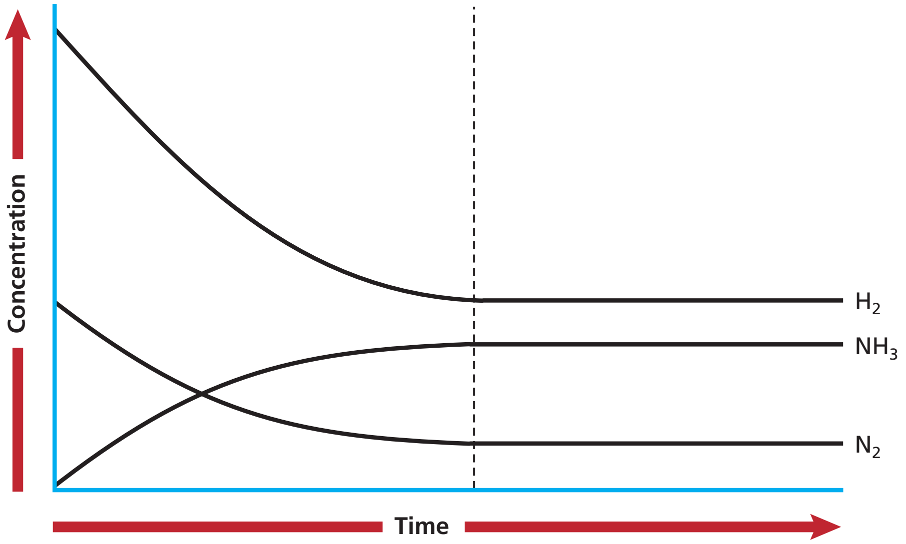
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta G^\circ = -33.1 \text{ kJ}$$

This reaction is important to agriculture because ammonia is used widely as a source of nitrogen for fertilizing corn and other farm crops. The photo on the opposite page shows ammonia being "knifed" into the soil.

Note that the equation for the production of ammonia has a negative standard free energy, ΔG°. Recall that a negative sign for ΔG° indicates that the

Figure 18-1

The concentrations of the reactants (H_2 and N_2) decrease at first while the concentration of the product (NH_3) increases. Then, before the reactants are used up, all concentrations become constant.



reaction is spontaneous under standard conditions. Standard conditions are defined as 298 K and one atmosphere pressure. But spontaneous reactions are not always fast. When carried out under standard conditions, this ammonia-forming reaction is much too slow. To produce ammonia at a rate that is practical, the reaction must be carried out at a much higher temperature than 298 K and a higher pressure than one atmosphere.

What happens when one mole of nitrogen and three moles of hydrogen, the amounts shown in the equation, are placed in a closed reaction vessel at 723 K? Because the reaction is spontaneous, nitrogen and hydrogen begin to react. **Figure 18-1** illustrates the progress of the reaction. Note that the concentration of the product, NH_3, is zero at the start and gradually increases with time. The reactants, H_2 and N_2, are consumed in the reaction, so their concentrations gradually decrease. After a period of time, however, the concentrations of H_2, N_2, and NH_3 no longer change. All concentrations become constant, as shown by the horizontal lines on the right side of the diagram. The concentrations of H_2 and N_2 are not zero, so not all of the reactants were converted to product even though $\Delta G°$ for this reaction is negative.

CHEMISTRY CD-ROM

Go to the **Chemistry Interactive CD-ROM** to find additional resources for this chapter.

Reversible reactions When a reaction results in almost complete conversion of reactants to products, chemists say that the reaction goes to completion. But most reactions, including the ammonia-forming reaction, do not go to completion. They appear to stop. The reason is that these reactions are reversible. A **reversible reaction** is one that can occur in both the forward and the reverse directions.

$$\text{Forward: } N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
$$\text{Reverse: } N_2(g) + 3H_2(g) \leftarrow 2NH_3(g)$$

Chemists combine these two equations into a single equation that uses a double arrow to show that both reactions occur.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

When you read the equation, the reactants in the forward reaction are on the left. In the reverse reaction, the reactants are on the right. In the forward reaction, hydrogen and nitrogen combine to form the product ammonia. In the reverse

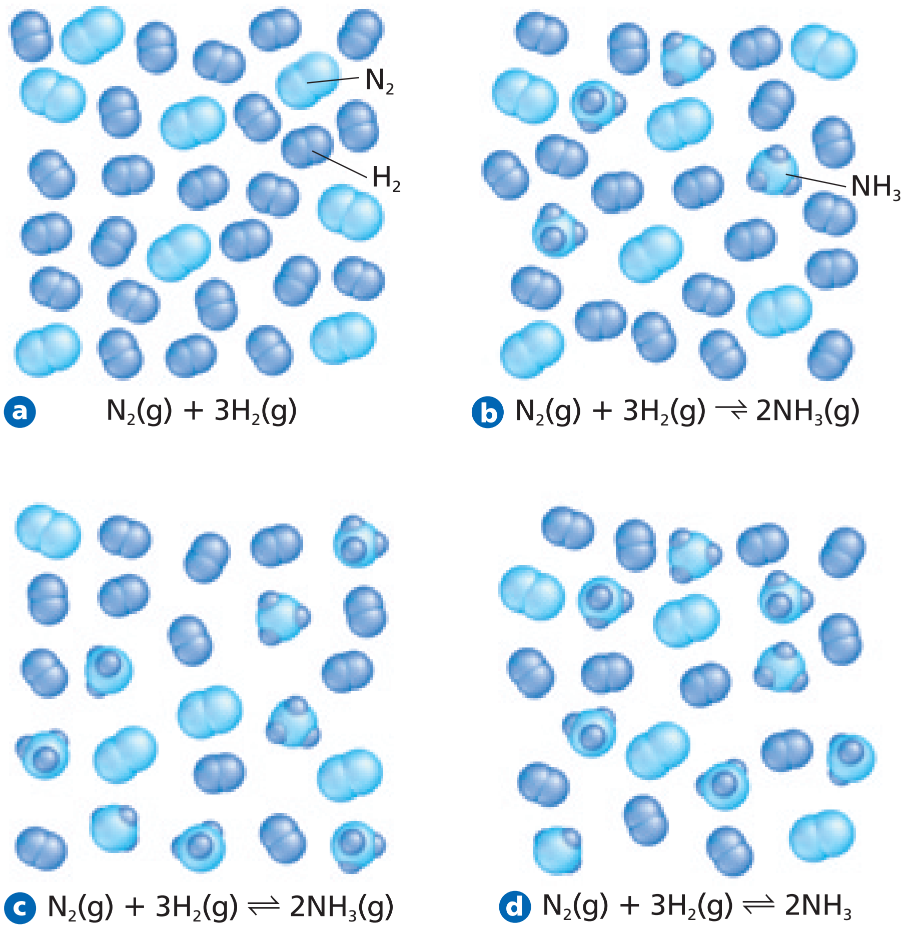


Figure 18-2

Only the forward reaction can occur in **a** because only the reactants are present. In **b**, the product, ammonia, is present and the reverse reaction begins. Compare **c** and **d**. Has equilibrium been established? Refer to **Table C-1** in Appendix C for a key to atom color correlations.

reaction, ammonia decomposes into the products hydrogen and nitrogen. How does the reversibility of this reaction affect the production of ammonia?

Figure 18-2a shows a mixture of nitrogen and hydrogen just as the reaction begins at a definite, initial rate. No ammonia is present so only the forward reaction can occur.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

As hydrogen and nitrogen combine to form ammonia, their concentrations decrease, as shown in **Figure 18-2b.** Recall from Chapter 17 that the rate of a reaction depends upon the concentration of the reactants. The decrease in the concentration of the reactants causes the rate of the forward reaction to decrease. As soon as ammonia is present, the reverse reaction can occur, slowly at first, but at an increasing rate as the concentration of ammonia increases.

$$N_2(g) + 3H_2(g) \leftarrow 2NH_3(g)$$

As the reaction proceeds, the rate of the forward reaction continues to decrease and the rate of the reverse reaction continues to increase until the two rates are equal. At that point, ammonia is being produced as fast as it is being decomposed, so the concentrations of nitrogen, hydrogen, and ammonia remain constant, as shown in **Figures 18-2c** and **18-2d.** The system has reached a state of balance or equilibrium. The word *equilibrium* means that opposing processes are in balance. **Chemical equilibrium** is a state in which the forward and reverse reactions balance each other because they take place at equal rates.

$$\text{Rate}_{\text{forward reaction}} = \text{Rate}_{\text{reverse reaction}}$$

Figure 18-3

If the only way in or out of San Francisco and Sausalito is across the Golden Gate Bridge, which joins the two cities, then the number of vehicles in the two cities will remain constant if the number of vehicles per hour crossing the bridge in one direction equals the number of vehicles crossing in the opposite direction. Will the same vehicles always be in the same city?

You can recognize that the ammonia-forming reaction reaches a state of chemical equilbrium because its chemical equation is written with a double arrow like this.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

At equilibrium, the concentrations of reactants and products are constant, as you saw in **Figures 18-2c** and **18-2d.** However, that doesn't mean that the amounts or concentrations of reactants and products are equal. That is seldom the case. In fact, it's not unusual for the equilibrium concentrations of a reactant and product to differ by a factor of one million or more.

The dynamic nature of equilibrium Equilibrium is a state of action, not inaction. For example, consider this analogy. The Golden Gate Bridge, shown in **Figure 18-3,** connects two California cities, San Francisco and Sausalito. Suppose that all roads leading into and out of the two cities are closed for a day—except the Golden Gate Bridge. In addition, suppose that the number of vehicles per hour crossing the bridge in one direction equals the number of vehicles per hour traveling in the opposite direction. Given these circumstances, the number of vehicles in each of the two cities remains constant even though vehicles continue to cross the bridge. In this analogy, note that the total numbers of vehicles in the two cities do not have to be equal. Equilibrium requires only that the number of vehicles crossing the bridge in one direction is equal to the number crossing in the opposite direction.

The dynamic nature of chemical equilibrium can be illustrated by placing equal masses of iodine crystals in two interconnected flasks, as shown in **Figure 18-4a.** The crystals in the flask on the left contain iodine molecules made up entirely of the nonradioactive isotope I-127. The crystals in the flask on the right contain iodine molecules made up of the radioactive isotope I-131. The Geiger counters indicate the radioactivity within each flask.

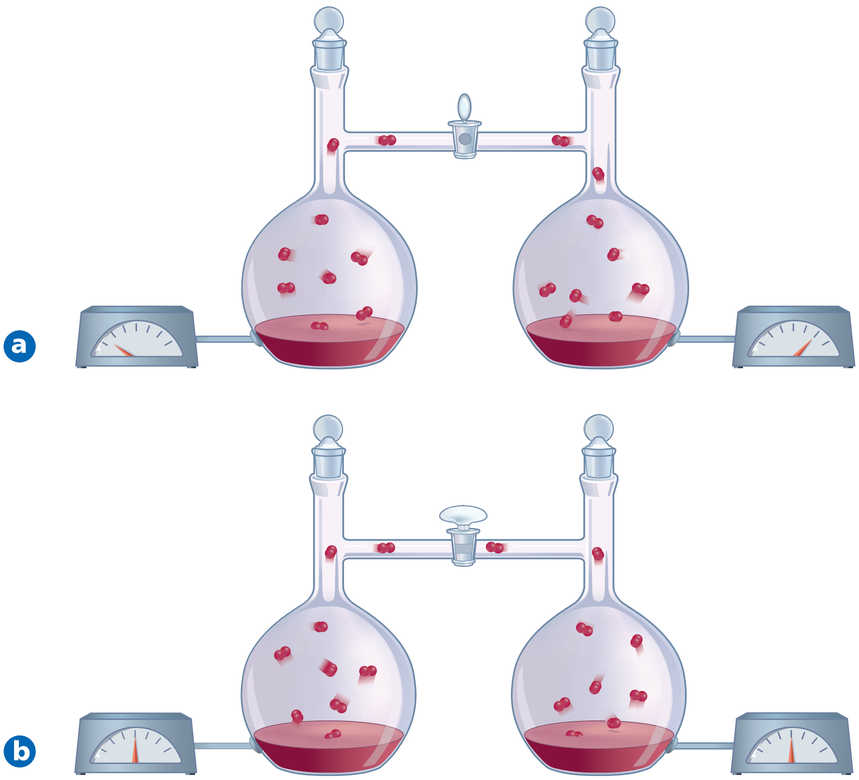


Figure 18-4

Radioactive iodine molecules from the solid in the flask on the right could not appear in the solid in the flask on the left unless iodine molecules were changing back and forth between the solid and gaseous phases.

Each flask is a closed system. No reactant or product can enter or leave. At 298 K and one atmosphere pressure, this equilibrium is established in both flasks.

$$I_2(s) \rightleftharpoons I_2(g)$$

In the forward process, called sublimation, iodine molecules change directly from the solid phase to the gas phase. In the reverse process, gaseous iodine molecules return to the solid phase. A solid-vapor equilibrium is established in each flask.

When the stopcock in the tube connecting the two flasks is opened, iodine vapor can travel back and forth between the two flasks. After a period of time, the readings on the Geiger counters indicate that the flask on the left contains as many radioactive I-131 molecules as the flask on the right *in both the vapor and the solid phases.* See **Figure 18-4b.** How could radioactive I-131 molecules that were originally in the crystals in the flask on the right become part of the crystals in the flask on the left? The evidence suggests that iodine molecules constantly change from the solid phase to the gas phase according to the forward process, and that gaseous iodine molecules convert back to the solid phase according to the reverse process.

Equilibrium Expressions and Constants

You have learned that some chemical systems have little tendency to react and others go readily to completion. In between these two extremes are the majority of reactions that reach a state of equilibrium with varying amounts of reactants unconsumed. If the reactants are not consumed, then not all the product predicted by the balanced chemical equation will be produced. According to the equation for the ammonia-producing reaction, two moles of ammonia should be produced when one mole of nitrogen and three moles of hydrogen react. Because the reaction reaches a state of equilibrium, however, fewer than two moles of ammonia will actually be obtained. Chemists need to be able to predict the yield of a reaction.

In 1864, the Norwegian chemists Cato Maximilian Guldberg and Peter Waage proposed the **law of chemical equilibrium,** which states that at a given temperature, a chemical system may reach a state in which a particular ratio of reactant and product concentrations has a constant value. For example, the general equation for a reaction at equilibrium can be written as follows.

$$aA + bB \rightleftharpoons cC + dD$$

A and B are the reactants; C and D the products. The coefficients in the balanced equation are *a, b, c,* and *d.* If the law of chemical equilibrium is applied to this reaction, the following ratio is obtained.

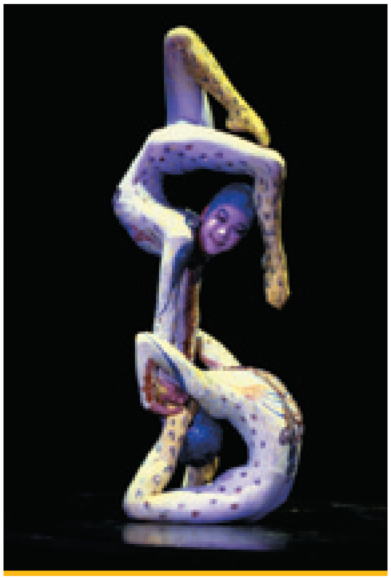
$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

This ratio is called the equilibrium constant expression. The square brackets indicate the molar concentrations of the reactants and products at equilibrium in mol/L. The **equilibrium constant,** K_{eq}, is the numerical value of the ratio of product concentrations to reactant concentrations, with each concentration raised to the power corresponding to its coefficient in the balanced equation. The value of K_{eq} is constant only at a specified temperature.

How can you interpret the size of the equilibrium constant? Recall that ratios, or fractions, with large numerators are larger numbers than fractions

Physics CONNECTION

In physics, a push or pull on an object is known as a force. Whenever someone pushes on a door, pulls on a dog's leash, or throws a ball, that person exerts a force. When two or more forces are exerted on the same object they add together. If the forces are exerted in opposite directions, one is essentially subtracted from the other. Thus, in a game of tug of war when two teams pull on a rope with equal force, the resulting force has a magnitude of zero. As a result, the object does not move and the system is said to be in equilibrium. Similarly, the acrobats below represent a system in equilibrium. Equal and opposite forces are called balanced forces. If, instead, one force is greater in magnitude than the other, the resulting force is greater than zero when the smaller force is subtracted from the greater one. The resulting force is called an unbalanced force, and an unbalanced force will cause an object to move.



with large denominators. For example, compare the ratio 5/1 with 1/5. Five is a larger number than one-fifth. Because the product concentrations are in the numerator of the equilibrium expression, a numerically large K_{eq} means that the equilibrium mixture contains more products than reactants. Similarly, a numerically small K_{eq} means that the equilibrium mixture contains more reactants than products.

$K_{eq} > 1$: More products than reactants at equilibrium.
$K_{eq} < 1$: More reactants than products at equilibrium.

Constants for homogeneous equilibria How would you write the equilibrium constant expression for this reaction in which hydrogen and iodine react to form hydrogen iodide?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

This reaction is a **homogeneous equilibrium,** which means that all the reactants and products are in the same physical state. All participants are gases. To begin writing the equilibrium constant expression, place the product concentration in the numerator and the reactant concentrations in the denominator.

$$\frac{[HI]}{[H_2][I_2]}$$

The expression becomes equal to K_{eq} when you add the coefficients from the balanced chemical equation as exponents.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

K_{eq} for this homogeneous equilibrium at 731 K is 49.7. Note that 49.7 has no units. In writing equilibrium constant expressions, it's customary to omit units. Considering the size of K_{eq}, are there more products than reactants present at equilibrium?

EXAMPLE PROBLEM 18-1

Equilibrium Constant Expressions for Homogeneous Equilibria

Write the equilibrium constant expression for the reaction in which ammonia gas is produced from hydrogen and nitrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

1. Analyze the Problem

You have been given the equation for the reaction, which provides the information needed to write the equilibrium constant expression. The equilibrium is homogeneous because the reactants and product are in the same physical state. The form of the equilibrium constant expression is $K_{eq} = \frac{[C]^c}{[A]^a[B]^b}$.

Known

$[C] = [NH_3]$	coefficient $NH_3 = 2$
$[A] = [N_2]$	coefficient $N_2 = 1$
$[B] = [H_2]$	coefficient $H_2 = 3$

Unknown

$K_{eq} = ?$

This plant for the manufacture of ammonia employs the Haber process, which maximizes the yield of ammonia by adjusting the temperature and pressure of the reaction.

2. Solve for the Unknown

Place the product concentration in the numerator and the reactant concentrations in the denominator.

$$\frac{[NH_3]}{[N_2][H_2]}$$

Raise the concentration of each reactant and product to a power equal to its coefficient in the balanced chemical equation and set the ratio equal to K_{eq}.

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

3. Evaluate the Answer

The product concentration is in the numerator and the reactant concentrations are in the denominator. Product and reactant concentrations are raised to powers equal to their coefficients.

PRACTICE PROBLEMS

1. Write equilibrium constant expressions for these equilibria.
- **a.** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- **b.** $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
- **c.** $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

Practice!

For more practice writing homogeneous equilibrium constant expressions, go to **Supplemental Practice Problems** in Appendix A.

Constants for heterogeneous equilibria You have learned to write K_{eq} expressions for homogeneous equilibria, those in which all reactants and products are in the same physical state. When the reactants and products of a reaction are present in more than one physical state, the equilibrium is called a **heterogeneous equilibrium.**

When ethanol is placed in a closed flask, a liquid-vapor equilibrium is established, as illustrated in **Figure 18-5.**

$$C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$$

To write the equilibrium constant expression for this process, you would form a ratio of the product to the reactant. At a given temperature, the ratio would have a constant value K.

$$K = \frac{[C_2H_5OH(g)]}{[C_2H_5OH(l)]}$$

Note that the term in the denominator is the concentration of liquid ethanol. Because liquid ethanol is a pure substance, its concentration is constant at a given temperature. That's because the concentration of a pure substance is its density in moles per liter. At any given temperature, density does not change. No matter how much or how little C_2H_5OH is present, its concentration remains constant. Therefore, the term in the denominator is a constant and can be combined with K.

$$K[C_2H_5OH(l)] = [C_2H_5OH(g)] = K_{eq}$$

The equilibrium constant expression for this phase change is

$$K_{eq} = [C_2H_5OH(g)]$$

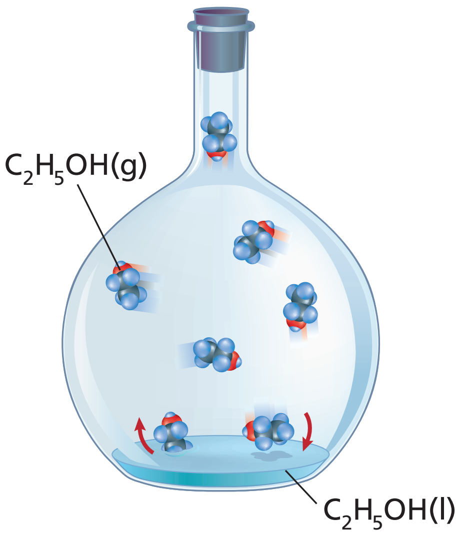


Figure 18-5

The rate of evaporation of ethanol equals the rate of condensation. This two-phase equilibrium is called a heterogeneous equilibrium. K_{eq} depends only on $[C_2H_5OH(g)]$.

Solids also are pure substances with unchanging concentrations, so equilibria involving solids can be simplified in the same way. For example, recall the experiment involving the sublimation of iodine crystals in **Figure 18-4** on page 562.

$$I_2(s) \rightleftharpoons I_2(g)$$

$$K_{eq} = [I_2(g)]$$

The equilibrium depends only on the concentration of gaseous iodine in the system.

EXAMPLE PROBLEM 18-2

Equilibrium Constant Expressions for Heterogeneous Equilibria

Write the equilibrium constant expression for the decomposition of baking soda (sodium hydrogen carbonate).

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

1. Analyze the Problem

You are given a heterogeneous equilibrium involving gases and solids. The general form of the equilibrium constant expression for this reaction is

$$K_{eq} = \frac{[C]^c[D]^d[E]^e}{[A]^a[B]^b}.$$

Because the reactant and one of the products are solids with constant concentrations, they can be omitted from the equilibrium constant expression.

Known

$[C] = [Na_2CO_3]$	coefficient $Na_2CO_3 = 1$
$[D] = [CO_2]$	coefficient $CO_2 = 1$
$[E] = [H_2O]$	coefficient $H_2O = 1$
$[A] = [NaHCO_3]$	coefficient $NaHCO_3 = 2$

Unknown

equilibrium constant expression = ?

Baking soda, or sodium hydrogen carbonate, makes this Irish soda bread light and airy. Baking soda is also useful as an antacid, a cleaner, and a deodorizer.

2. Solve for the Unknown

Write a ratio with the concentrations of the products in the numerator and the concentration of the reactant in the denominator.

$$\frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]}$$

Leave out $[NaHCO_3]$ and $[Na_2CO_3]$ because they are solids.

$$[CO_2][H_2O]$$

Because the coefficients of $[CO_2]$ and $[H_2O]$ are 1, the expression is complete.

$$K_{eq} = [CO_2][H_2O]$$

3. Evaluate the Answer

The expression correctly applies the law of chemical equilibrium to the equation.

PRACTICE PROBLEMS

2. Write equilibrium constant expressions for these heterogeneous equilibria.
   a. $C_{10}H_8(s) \rightleftharpoons C_{10}H_8(g)$
   b. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
   c. $H_2O(l) \rightleftharpoons H_2O(g)$
   d. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
   e. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

Practice!

For more practice writing heterogeneous equilibrium constant expressions, go to Supplemental Practice Problems in Appendix A.

Determining the Value of Equilibrium Constants

For a given reaction at a given temperature, K_{eq} will always be the same regardless of the initial concentrations of reactants and products. To test the truth of this statement, three experiments were carried out to investigate this reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The results are summarized in **Table 18-1.** In trial 1, 1.0000 mol H_2 and 2.0000 mol I_2 are placed in a 1.0000-L vessel. These initial concentrations have the symbols $[H_2]_0$ and $[I_2]_0$. No HI is present at the beginning of trial 1. In trial 2, only HI is present at the start of the experiment. In trial 3, each of the three participants has the same initial concentration.

When equilibrium is established, the concentration of each substance is determined experimentally. In **Table 18-1,** the symbol $[HI]_{eq}$ represents the concentration of HI at equilibrium. Note that the equilibrium concentrations are not the same in the three trials, yet when each set of equilibrium concentrations is put into the equilibrium constant expression, the value of K_{eq} is the same. Each set of equilibrium concentrations represents an equilibrium position. Although an equilibrium system has only one value for K_{eq} at a particular temperature, it has an unlimited number of equilibrium positions. Equilibrium positions depend upon the initial concentrations of the reactants and products.

The large value of K_{eq} for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ means that at equilibrium the product is present in larger amount than the reactants. Many equilibria, however, have small K_{eq} values. Do you remember what this means? K_{eq} for the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ equals 4.6×10^{-31} at 298 K. A K_{eq} this small means that the product, NO, is practically nonexistent at equilibrium.

Table 18-1

Three Experiments for an Equilibrium System

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 731 K

Trial	$[H_2]_0$ (M)	$[I_2]_0$ (M)	$[HI]_0$ (M)	$[H_2]_{eq}$ (M)	$[I_2]_{eq}$ (M)	$[HI]_{eq}$ (M)	$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$
1	1.0000	2.0000	0.0	0.06587	1.0659	1.8682	$\frac{[1.8682]^2}{[0.06587][1.0659]} = 49.70$
2	0.0	0.0	5.0000	0.5525	0.5525	3.8950	$\frac{[3.8950]^2}{[0.5525][0.5525]} = 49.70$
3	1.0000	1.0000	1.0000	0.2485	0.2485	1.7515	$\frac{[1.7515]^2}{[0.2485][0.2485]} = 49.70$

Math Handbook

Review solving algebraic equations in the **Math Handbook** on page 897 of this text.

EXAMPLE PROBLEM 18-3

Calculating the Value of Equilibrium Constants

Calculate the value of K_{eq} for the equilibrium constant expression $K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$ given concentration data at one equilibrium position: $[NH_3] = 0.933$ mol/L, $[N_2] = 0.533$ mol/L, $[H_2] = 1.600$ mol/L.

1. Analyze the Problem

You have been given the equilibrium constant expression and the concentration of each reactant and product. You must calculate the equilibrium constant. Because the reactant, H_2, has the largest concentration and is raised to the third power in the denominator, K_{eq} is likely to be less than 1.

Known

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$[NH_3] = 0.933$ mol/L

$[N_2] = 0.533$ mol/L

$[H_2] = 1.600$ mol/L

Unknown

$K_{eq} = ?$

2. Solve for the Unknown

Substitute the known values into the equilibrium constant expression and calculate its value.

$$K_{eq} = \frac{[0.933]^2}{[0.533][1.600]^3} = 0.399$$

3. Evaluate the Answer

The smallest number of significant figures in the given data is three. Therefore, the answer is correctly stated with three digits. The calculation is correct and, as predicted, the value of K_{eq} is less than 1.

PRACTICE PROBLEMS

3. Calculate K_{eq} for the equilibrium in Practice Problem 1a on page 565 using the data $[N_2O_4] = 0.0185$ mol/L and $[NO_2] = 0.0627$ mol/L.

4. Calculate K_{eq} for the equilibrium in Practice Problem 1b on page 565 using the data $[CO] = 0.0613$ mol/L, $[H_2] = 0.1839$ mol/L, $[CH_4] = 0.0387$ mol/L, and $[H_2O] = 0.0387$ mol/L.

Practice!

For more practice evaluating quotients, go to **Supplemental Practice Problems** in Appendix A.

Section 18.1 Assessment

5. How does the concept of reversibility explain the establishment of equilibrium?

6. What characteristics define a system at equilibrium?

7 When you write an equilibrium constant expression, how do you decide what goes in the numerator and in the denominator?

8. **Thinking Critically** Determine whether the following statement is correct: When chemical equilibrium exists, the reactant and product concentrations remain constant and the forward and reverse reactions cease. Explain your answer.

9. **Using Numbers** Determine the value of K_{eq} at 400 K for the decomposition of phosphorus pentachloride if $[PCl_5] = 0.135$ mol/L, $[PCl_3] = 0.550$ mol/L, and $[Cl_2] = 0.550$ mol/L. The equation for the reaction is: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Section 18.2

Factors Affecting Chemical Equilibrium

Manufacturers are aware that it makes good sense to minimize waste by finding ways of using leftover materials. Manufacturing new products from byproducts adds to profits and eliminates the problem of disposing of waste without causing environmental damage. What part does equilibrium play in promoting cost-cutting efficiency?

Objectives

- **Describe** how various factors affect chemical equilibrium.
- **Explain** how Le Châtelier's principle applies to equilibrium systems.

Vocabulary

Le Châtelier's principle

Le Châtelier's Principle

Suppose that the byproducts of an industrial process are the gases carbon monoxide and hydrogen and a company chemist believes these gases can be combined to produce the fuel methane (CH_4) using this reaction.

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \quad \Delta H^\circ = -206.5 \text{ kJ}$$

When the industrial chemist places CO and H_2 in a closed reaction vessel at 1200 K, the reaction establishes this equilibrium position (equilibrium position 1).

$$\begin{array}{ccccccc} CO(g) & + & 3H_2(g) & \rightleftharpoons & CH_4(g) & + & H_2O(g) \\ 0.30000M & & 0.10000M & & 0.05900M & & 0.02000M \end{array}$$

Inserting these concentrations into the equilibrium expression gives an equilibrium constant equal to 3.933.

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{(0.05900)(0.02000)}{(0.30000)(0.10000)^3} = 3.933$$

Unfortunately, a methane concentration of 0.05900 mol/L in the equilibrium mixture is too low to be of any practical use. Can the chemist change the equilibrium position and thereby increase the amount of methane?

In 1888, the French chemist Henri-Louis Le Châtelier discovered that there are ways to control equilibria to make reactions, including this one, more productive. He proposed what is now called **Le Châtelier's principle:** If a stress is applied to a system at equilibrium, the system shifts in the direction that relieves the stress. A stress is any kind of change in a system at equilibrium that upsets the equilibrium. You can use Le Châtelier's principle to predict how changes in concentration, volume (pressure), and temperature affect equilibrium. Changes in volume and pressure are interrelated because decreasing the volume of a reaction vessel at constant temperature increases the pressure inside. Conversely, increasing the volume decreases the pressure.

Careers Using Chemistry

Nurse Anesthetist

Would you like to work in a hospital operating room, helping patients remain pain-free during surgery? If so, consider a career as a nurse anesthetist.

In two-thirds of rural hospitals, nurse anesthetists provide all anesthesia services. In city hospitals, they work under anesthesiologists. These nurses also work in outpatient clinics and physicians' offices. As they regulate the anesthetic, they monitor body functions to make sure they stay in balance and the patient stays out of danger.

Changes in concentration What happens if the industrial chemist injects additional carbon monoxide into the reaction vessel, raising the concentration of carbon monoxide from 0.30000*M* to 1.00000*M*? The higher carbon monoxide concentration immediately increases the number of effective collisions between CO and H_2 molecules and unbalances the equilibrium. The rate of the forward reaction increases, as indicated by the longer arrow to the right.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

In time, the rate of the forward reaction slows down as the concentrations of CO and H_2 decrease. Simultaneously, the rate of the reverse reaction increases as more and more CH_4 and H_2O molecules are produced. Eventually, a new equilibrium position (position 2) is established with these concentrations.

$$\begin{array}{ccccccc} CO(g) & + & 3H_2(g) & \rightleftharpoons & CH_4(g) & + & H_2O(g) \\ 0.99254M & & 0.07762M & & 0.06648M & & 0.02746M \end{array}$$

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{(0.06648)(\ 0.02746)}{(0.99254)(0.07762)^3} = 3.933$$

Note that although K_{eq} has not changed, the new equilibrium position results in the desired effect—an increased concentration of methane. The results of this experiment are summarized in **Table 18-2.**

Table 18-2

Two Equilibrium Positions for the Equilibrium

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Equilibrium position	$[CO]_{eq}$ M	$[H_2]_{eq}$ M	$[CH_4]_{eq}$ M	$[H_2O]_{eq}$ M	K_{eq} M
1	0.30000	0.10000	0.05900	0.02000	3.933
2	0.99254	0.07762	0.06648	0.02746	3.933

Could you have predicted this result using Le Châtelier's principle? Yes. Think of the increased concentration of CO as a stress on the equilibrium. The equilibrium system reacts to the stress by consuming CO at an increased rate. This response, called a shift to the right, forms more CH_4 and H_2O. Any increase in the concentration of a reactant results in a shift to the right and additional product.

Suppose that rather than injecting more reactant, the chemist decides to remove a product (H_2O) by adding a desiccant to the reaction vessel. Recall from Chapter 11 that a desiccant is a substance that absorbs water. What does Le Châtelier's principle predict the equilibrium will do in response to a decrease in the concentration of water (the stress)? You are correct if you said that the equilibrium shifts in the direction that will tend to bring the concentration of water back up. That is, the equilibrium shifts to the right and results in additional product.

It might be helpful to think about the produce vendor in **Figure 18-6** who wants to keep a display of vegetables looking neat and tempting. The vendor must constantly add new vegetables to fill the empty spaces created when customers buy the vegetables. Similarly, the equilibrium reaction attempts to restore the lost water by producing more water. As a result, more water and more methane are produced. In any equilibrium, the removal of a product results in a shift to the right and the production of more product.

The equilibrium position also can be shifted to the left, toward the reactants. Do you have an idea how? Le Châtelier's principle predicts that if additional product is added to a reaction at equilibrium, the reaction will shift to the left. The stress is relieved by converting products to reactants. If one of the reactants is removed, a similar shift to the left will occur.

When predicting the results of a stress on an equilibrium using Le Châtelier's principle, it is important to have the equation for the reaction in

Figure 18-6

A neat arrangement of produce can be thought of as being at equilibrium—nothing is changing. But when a customer buys some of the vegetables, the equilibrium is disturbed. The produce vendor then restores equilibrium by filling the empty spots.

CONTENTS

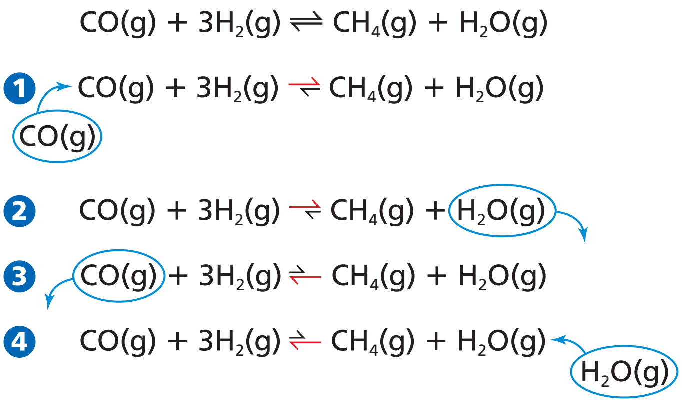


Figure 18-7

The addition or removal of a reactant or product shifts the equilibrium in the direction that relieves the stress. Note the unequal arrows, which indicate the direction of the shift. How would the reaction shift if you added H_2? Removed CH_4?

view. The effects of changing concentration are summarized in **Figure 18-7.** Refer to this figure as you practice applying Le Châtelier's principle.

Changes in volume Consider again the reaction for making methane from byproduct gases.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

Can this reaction be forced to produce more methane by changing the volume of the reaction vessel? Suppose the vessel's volume can be changed using a piston-like device similar to the one shown in **Figure 18-8.** If the piston is forced downward, the volume of the system decreases. You have learned that Boyle's law says that decreasing the volume at constant temperature increases the pressure. The increased pressure is a stress on the reaction at equilibrium. How does the equilibrium respond to the disturbance and relieve the stress?

Recall that the pressure exerted by an ideal gas depends upon the number of gas particles that collide with the walls of the vessel. The more gas particles contained in the vessel, the greater the pressure. If the number of gas particles is increased at constant temperature, the pressure of the gas increases. Similarly, if the number of gas particles is decreased, the pressure also decreases. How does this relationship between numbers of gas particles and pressure apply to the reaction for making methane? Compare the number of moles of gaseous reactants in the equation with the number of moles of gaseous products. For every two moles of gaseous products (1 mol CH_4 and 1 mol H_2O), four moles of gaseous reactants are consumed (1 mol CO and 3 mol H_2), a net decrease of two moles. If you apply Le Châtelier's principle, you can see that the equilibrium can relieve the stress of increased pressure by shifting to the right. This shift decreases the total number of moles of gas and thus, the pressure inside the reaction vessel decreases. Although the shift to the right does not reduce the pressure to its original value, it has the desired effect—the equilibrium produces more methane. See **Figure 18-8.**

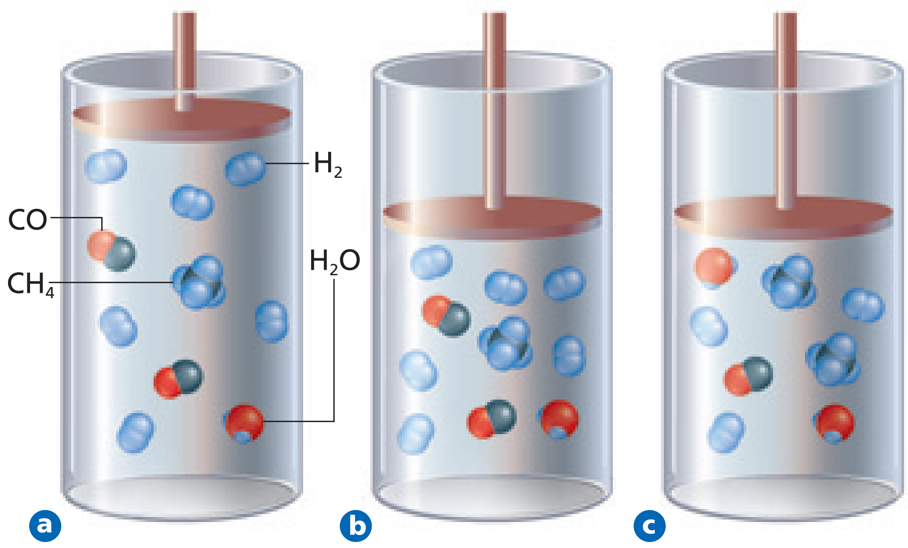


Figure 18-8

In a, the reaction between CO and H_2 is at equilibrium. In b, the piston has been lowered decreasing the volume and increasing the pressure. The outcome is seen in c. More molecules of the products have formed. Their formation helped relieve the stress on the system. How do the numbers of particles in a and c compare?

Changing the volume (and pressure) of an equilibrium system shifts the equilibrium only if the number of moles of gaseous reactants is different from the number of moles of gaseous products. Changing the volume of a reaction vessel containing the equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ would cause no shift in the equilibrium because the number of moles of gas is the same on both sides of the equation.

Changes in temperature You have now learned that changes in concentration and volume change the equilibrium position by causing shifts to the right or left, but they do not change the equilibrium constant. A change in temperature, however, alters both the equilibrium position and the equilibrium constant. To understand how a change in temperature affects an equilibrium, recall that virtually every chemical reaction is either endothermic or exothermic. For example, the reaction for making methane has a negative $\Delta H°$, which means that the forward reaction is exothermic and the reverse reaction is endothermic.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad \Delta H° = -206.5 \text{ kJ}$$

Heat can be thought of as a product in the forward reaction and a reactant in the reverse reaction. You can see this by reading the equation forward and backward.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + \text{heat}$$

How could an industrial chemist regulate the temperature to increase the amount of methane in the equilibrium mixture? According to Le Châtelier's principle, if heat is added, the reaction shifts in the direction in which heat is used up; that is, the reaction shifts to the left. A shift to the left means a decrease in the concentration of methane because methane is a reactant in the reverse reaction. However, lowering the temperature shifts the equilibrium to the right because the forward reaction liberates heat and relieves the stress. In shifting to the right, the equilibrium produces more methane.

Any change in temperature results in a change in K_{eq}. Recall that the larger the value of K_{eq}, the more product is found in the equilibrium mixture. Thus, for the methane-producing reaction, K_{eq} increases in value when the temperature is lowered and decreases when the temperature is raised.

Figure 18-9 shows how another equilibrium responds to changes in temperature. The endothermic equilibrium is described by this equation.

$$\text{heat} + \underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l)$$

Figure 18-9

At room temperature, the solution in **a** is an equilibrium mixture of pink reactants and blue products. When the temperature is lowered in **b**, this endothermic reaction shifts toward the pink reactants. In **c**, the stress of higher temperature causes the reaction to shift toward the blue products.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + heat \leftarrow \text{heat}$$

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) + \text{heat} \rightarrow$$

$$\text{heat} \rightarrow heat + Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

$$\leftarrow \text{heat} + Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

Figure 18-10

For the exothermic reaction between CO and H_2, raising the temperature shifts the equilibrium to the left (top equation). Lowering the temperature results in a shift to the right (second equation). The opposite is true for the endothermic reaction involving cobalt and chloride ions (third and last equations).

At room temperature, this mixture of aqueous ions appears violet because it contains significant amounts of pink $Co(H_2O)_6^{2+}(aq)$ and blue $CoCl_4^{2-}(aq)$. When cooled in an ice bath, the equilibrium mixture turns pink. The removal of heat is a stress on the equilibrium. The stress is relieved by an equilibrium shift to the left, generating more heat and producing more pink $Co(H_2O)_6^{2+}$ ions. When heat is added, the equilibrium mixture appears blue because the equilibrium shifts to the right to absorb the additional heat. As a result, more blue $CoCl_4^{2-}$ ions are created. You can investigate this equilibrium system further in the **miniLAB** below. The diagram in **Figure 18-10** shows the effect of heating and cooling on exothermic and endothermic reactions.

Changes in concentration, volume, and temperature make a difference in the amount of product formed in a reaction. Can a catalyst also affect product concentration? A catalyst speeds up a reaction, but it does so equally in both directions. Therefore, a catalyzed reaction reaches equilibrium more quickly, but with no change in the amount of product formed. Read the **Chemistry and Technology** feature at the end of this chapter to learn how Le Châtelier's principle is applied to an important industrial process.

miniLAB

Shifts in Equilibrium

Observing and Inferring Le Châtelier's principle states that if a stress is placed on a reaction at equilibrium, the system will shift in a way that will relieve the stress. In this experiment, you will witness an equilibrium shift in a colorful way.

Materials test tubes (2); 10-mL graduated cylinder; 250-mL beaker; concentrated hydrochloric acid; 0.1*M* $CoCl_2$ solution; ice bath; table salt; hot plate

Procedures

1. Place about 2 mL of 0.1*M* $CoCl_2$ solution in a test tube. Record the color of the solution.
2. Add about 3 mL of concentrated HCl to the test tube. Record the color of the solution. **CAUTION:** *HCl can burn skin and clothing.*
3. Add enough water to the test tube to make a color change occur. Record the color.
4. Add about 2 mL of 0.1*M* $CoCl_2$ to another test tube. Add concentrated HCl dropwise until the solution turns purple. If the solution becomes blue, add water until it turns purple.
5. Place the test tube in an ice bath that has had some salt sprinkled into the ice water. Record the color of the solution in the test tube.
6. Place the test tube in a hot water bath that is at least 70°C. Record the color of the solution.

Analysis

1. The equation for the reversible reaction in this experiment is

   $$\underset{\text{pink}}{Co(H_2O)_6^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}} + 6H_2O$$

   Use the equation to explain your observations of color in steps 1–3.
2. Explain how the equilibrium shifts when energy is added or removed.

A biological equilibrium If you have ever traveled to the mountains for a strenuous activity such as skiing, hiking, or mountain climbing, it is likely that you have felt tired and lightheaded for a time. This feeling is a result of the fact that at high altitudes, the air is thinner and contains fewer oxygen molecules. An important equilibrium in your body is disturbed. That equilibrium is represented by the following equation.

$$Hgb(aq) + O_2(g) \rightleftharpoons Hgb(O_2)(aq)$$

Hgb and $Hgb(O_2)$ are greatly simplified formulas for hemoglobin and oxygenated hemoglobin, respectively. Hemoglobin is the blood protein that transports oxygen from your lungs to your muscles and other tissues where it is used in the metabolic processes that produce energy. What happens to this equilibrium at an altitude where both the atmospheric pressure and oxygen concentration are lower than normal for your body? Applying Le Châtelier's principle, the equilibrium shifts to the left to produce more oxygen. This shift reduces the amount of $Hgb(O_2)$ in your blood and, therefore, the supply of oxygen to your muscles and other tissues.

After spending some time in the mountains, you probably noticed that your fatigue lessened. That's because your body adapted to the reduced oxygen concentration by producing more Hgb, which shifts the equilibrium back to the right and increases the amount of $Hgb(O_2)$ in your blood. The Sherpas in **Figure 18-11,** who live and work in the mountains, do not experience discomfort because the equilibrium systems in their blood are adapted to high-altitude conditions.

Figure 18-11

The equilibrium in the blood of Sherpas is adjusted to the lower level of oxygen in the air at high altitudes. Do you think Sherpas would experience a period of adjustment if they moved to sea level?

Section 18.2 Assessment

10. How does a system at equilibrium respond to a stress? What factors are considered to be stresses on an equilibrium system?

11. Use Le Châtelier's principle to predict how each of these changes would affect the ammonia equilibrium system.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

a. removing hydrogen from the system

b. adding ammonia to the system

c. adding hydrogen to the system

12. How would decreasing the volume of the reaction vessel affect each of these equilibria?

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

b. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

c. $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

13. In the following equilibrium, would you raise or lower the temperature to obtain these results?

$$C_2H_2(g) + H_2O(g) \rightleftharpoons CH_3CHO(g) \quad \Delta H° = -151 \text{ kJ}$$

a. an increase in the amount of CH_3CHO

b. a decrease in the amount of C_2H_2

c. an increase in the amount of H_2O

14. Thinking Critically Why does changing the volume of the reaction vessel have no effect on this equilibrium?

$$CO(g) + Fe_3O_4(s) \rightleftharpoons CO_2(g) + 3FeO(s)$$

15. Predicting Predict how this equilibrium would respond to a simultaneous increase in both temperature and pressure.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \quad \Delta H° = -220 \text{ kJ}$$

Section 18.3 Using Equilibrium Constants

Objectives

- **Determine** equilibrium concentrations of reactants and products.
- **Calculate** the solubility of a compound from its solubility product constant.
- **Explain** the common ion effect.

Vocabulary

solubility product constant
common ion
common ion effect

When a reaction has a large K_{eq}, the products are favored at equilibrium. That means that the equilibrium mixture contains more products than reactants. Conversely, when a reaction has a small K_{eq}, the reactants are favored at equilibrium, which means that the equilibrium mixture contains more reactants than products. Knowing the size of the equilibrium constant can help a chemist decide whether a reaction is practical for making a particular product.

Calculating Equilibrium Concentrations

The equilibrium constant expression can be useful in another way. Knowing the equilibrium constant expression, a chemist can calculate the equilibrium concentration of any substance involved in a reaction if the concentrations of all other reactants and products are known.

Suppose the industrial chemist that you read about earlier knows that at 1200 K, K_{eq} equals 3.933 for the reaction that forms methane from H_2 and CO. How much methane would actually be produced? If the concentrations of H_2, CO, and H_2O are known, the concentration of CH_4 can be calculated.

$$\begin{array}{ccccccccc} CO(g) & + & 3H_2(g) & \rightleftharpoons & CH_4(g) & + & H_2O(g) \\ 0.850M & & 1.333\ M & & ?M & & 0.286M \end{array}$$

The first thing the chemist would do is write the equilibrium constant expression.

$$K_{eq} = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

The equation can be solved for the unknown $[CH_4]$ by multiplying both sides of the equation by $[CO][H_2]^3$ and dividing both sides by $[H_2O]$.

$$[CH_4] = K_{eq} \times \frac{[CO][H_2]^3}{[H_2O]}$$

All the known concentrations and the value of K_{eq} (3.933) can now be substituted into the equilibrium constant expression.

$$[CH_4] = 3.933 \times \frac{(0.850)(1.333)^3}{(0.286)} = 27.7\ \text{mol/L}$$

The equilibrium concentration of CH_4 is 27.7 mol/L.

At this point an industrial chemist would evaluate whether an equilibrium concentration of 27.7 mol/L was sufficient to make the conversion of waste CO and H_2 to methane practical. Methane is becoming the fuel of choice for heating homes and cooking food. It is also the raw material for the manufacture of many products including acetylene and formic acid. Increasingly, it is being used as the energy source of fuel cells. At present, methane is relatively inexpensive but as demand grows, the cost will increase. Can the cost of a process which produces 27.7 mol/L CH_4 compete with the cost of obtaining methane from underground deposits? This is an important question for the manufacturer. **Figure 18-12** shows a surprising source of methane in the atmosphere.

Figure 18-12

As termites relentlessly digest cellulose (wood) throughout the world, they produce methane gas, which enters the atmosphere. Although now present in comparatively small amounts, methane is counted as one of the greenhouse gases.

Math Handbook

Review solving algebraic equations in the **Math Handbook** on page 897 of this text.

EXAMPLE PROBLEM 18-4

Calculating Equilibrium Concentrations

At 1405 K, hydrogen sulfide, also called rotten egg gas because of its bad odor, decomposes to form hydrogen and a diatomic sulfur molecule, S_2. The equilibrium constant for the reaction is 2.27×10^{-3}.

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

What is the concentration of hydrogen gas if $[S_2] = 0.0540$ mol/L and $[H_2S] = 0.184$ mol/L?

1. Analyze the Problem

You have been given K_{eq} and two of the three variables in the equilibrium constant expression. The equilibrium expression can be solved for $[H_2]$. K_{eq} is less than one, so more reactants than products are in the equilibrium mixture. Thus, you can predict that $[H_2]$ will be less than 0.184 mol/L, the concentration of the reactant H_2S.

Known	Unknown
$K_{eq} = 2.27 \times 10^{-3}$	$[H_2] = ?$ mol/L
$[S_2] = 0.0540$ mol/L	
$[H_2S] = 0.184$ mol/L	

2. Solve for the Unknown

Write the equilibrium constant expression.

$$\frac{[H_2]^2[S_2]}{[H_2S]^2} = K_{eq}$$

Solve the equation for $[H_2]^2$ by dividing both sides of the equation by $[S_2]$ and multiplying both sides by $[H_2S]^2$.

$$[H_2]^2 = K_{eq} \times \frac{[H_2S]^2}{[S_2]}$$

Substitute the known quantities into the expression and solve for $[H_2]$.

$$[H_2]^2 = 2.27 \times 10^{-3} \times \frac{(0.184)^2}{(0.0540)} = 1.42 \times 10^{-3}$$

$$[H_2] = \sqrt{1.42 \times 10^{-3}} = 0.0377 \text{ mol/L}$$

The equilibrium concentration of H_2 is 0.0377 mol/L.

3. Evaluate the Answer

All of the data for the problem have three significant figures, so the answer is correctly stated with three digits. As predicted, the equilibrium concentration of H_2 is less than 0.184 mol/L.

PRACTICE PROBLEMS

16. At a certain temperature, $K_{eq} = 10.5$ for the equilibrium

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Calculate these concentrations:

a. [CO] in an equilibrium mixture containing 0.933mol/L H_2 and 1.32 mol/L CH_3OH

b. $[H_2]$ in an equilibrium mixture containing 1.09 mol/L CO and 0.325 mol/L CH_3OH

c. $[CH_3OH]$ in an equilibrium mixture containing 0.0661 mol/L H_2 and 3.85 mol/L CO.

Practice!

For more practice calculating concentrations from the equilibrium constant expression, go to **Supplemental Practice Problems** in Appendix A.

Figure 18-13

The briney taste of a pickle is a great accompaniment for a deli sandwich. But the main purpose of the salt is to preserve the pickle. Can you think of other foods that are preserved by salting?

Solubility Equilibria

Some ionic compounds dissolve readily in water and some barely dissolve at all. Sodium chloride, or table salt, is typical of the soluble ionic compounds. On dissolving, all ionic compounds dissociate into ions.

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Approximately 36 g NaCl dissolves in 100 mL of water at 273 K. Without this high solubility, sodium chloride couldn't flavor and preserve foods like the pickles shown in **Figure 18-13.** Sodium chloride's vital role as an electrolyte in blood chemistry also depends upon its high solubility.

Although high solubility in water is often beneficial, low solubility also is important in many applications. For example, although barium ions are toxic to humans, patients are required to ingest barium sulfate prior to having an X ray of the digestive tract taken. X rays taken without barium sulfate in the digestive system are not well defined. Why can patients safely ingest barium sulfate?

In water solution, barium sulfate dissociates according to this equation.

$$BaSO_4(s) \rightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

As soon as the first product ions form, the reverse reaction begins to re-form the reactants according to this equation.

$$BaSO_4(s) \leftarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

With time, the rate of the reverse reaction becomes equal to the rate of the forward reaction and equilibrium is established.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

For sparingly soluble compounds, such as $BaSO_4$, the rates become equal when the concentrations of the aqueous ions are exceedingly small. Nevertheless, the solution at equilibrium is a saturated solution.

The equilibrium constant expression for the dissolving of $BaSO_4$ is

$$K_{eq} = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

In the equilibrium expression, $[BaSO_4]$ is constant because barium sulfate is a solid. This constant value is combined with K_{eq} by multiplying both sides of the equation by $[BaSO_4]$.

Figure 18-14

The presence of barium ions in the gastrointestinal system made the sharp definition of this X ray possible.

$$K_{eq} \times [BaSO_4] = [Ba^{2+}][SO_4^{2-}]$$

The product of K_{eq} and the concentration of the undissolved solid creates a new constant called the solubility product constant, K_{sp}. The **solubility product constant** is an equilibrium constant for the dissolving of a sparingly soluble ionic compound in water. The solubility product constant expression is

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} \text{ at 298 K}$$

The solubility product constant expression is the product of the concentrations of the ions each raised to the power equal to the coefficient of the ion in the chemical equation. The small value of K_{sp} indicates that products are not favored at equilibrium. Thus, few barium ions are present at equilibrium ($1.0 \times 10^{-5}M$) and a patient can safely ingest a barium sulfate solution to obtain a clear X ray like the one shown in **Figure 18-14.**

Here is another example.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

K_{sp} depends only on the concentrations of the ions in the saturated solution. However, to establish an equilibrium system, some undissolved solid, no matter how small the amount, must be present in the equilibrium mixture.

The solubility product constants for some ionic compounds are listed in **Table 18-3.** Note that they are all small numbers. Solubility product constants are measured and recorded only for sparingly soluble compounds.

Using solubility product constants The solubility product constants in **Table 18-3** have been determined through careful experiments. K_{sp} values are important because they can be used to determine the solubility of a sparingly soluble compound. Recall that the solubility of a compound in water is the amount of the substance that will dissolve in a given volume of water.

Table 18-3

Solubility Product Constants at 298 K

Compound	K_{sp}	Compound	K_{sp}	Compound	K_{sp}
Carbonates		**Halides**		**Hydroxides**	
$BaCO_3$	2.6×10^{-9}	CaF_2	3.5×10^{-11}	$Al(OH)_3$	4.6×10^{-33}
$CaCO_3$	3.4×10^{-9}	$PbBr_2$	6.6×10^{-6}	$Ca(OH)_2$	5.0×10^{-6}
$CuCO_3$	2.5×10^{-10}	$PbCl_2$	1.7×10^{-5}	$Cu(OH)_2$	2.2×10^{-20}
$PbCO_3$	7.4×10^{-14}	PbF_2	3.3×10^{-8}	$Fe(OH)_2$	4.9×10^{-17}
$MgCO_3$	6.8×10^{-6}	PbI_2	9.8×10^{-9}	$Fe(OH)_3$	2.8×10^{-39}
Ag_2CO_3	8.5×10^{-12}	AgCl	1.8×10^{-10}	$Mg(OH)_2$	5.6×10^{-12}
$ZnCO_3$	1.5×10^{-10}	AgBr	5.4×10^{-13}	$Zn(OH)_2$	3×10^{-17}
Hg_2CO_3	3.6×10^{-17}	AgI	8.5×10^{-17}	**Sulfates**	
Chromates		**Phosphates**		$BaSO_4$	1.1×10^{-10}
$BaCrO_4$	1.2×10^{-10}	$AlPO_4$	9.8×10^{-21}	$CaSO_4$	4.9×10^{-5}
$PbCrO_4$	2.3×10^{-13}	$Ca_3(PO_4)_2$	2.1×10^{-33}	$PbSO_4$	2.5×10^{-8}
Ag_2CrO_4	1.1×10^{-12}	$Mg_3(PO_4)_2$	1.0×10^{-24}	Ag_2SO_4	1.2×10^{-5}

CONTENTS

Suppose you wish to determine the solubility of silver iodide (AgI) in mol/L at 298 K. The equilibrium equation and solubility product constant expression are

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$
$$K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17} \text{ at } 298 \text{ K}$$

The first thing you should do is let the symbol s represent the solubility of AgI; that is, the number of moles of AgI that dissolves in a liter of solution. The equation indicates that for every mole of AgI that dissolves, an equal number of moles of Ag^+ ions forms in solution. Therefore, $[Ag^+]$ equals s. Every Ag^+ has an accompanying I^- ion, so $[I^-]$ also equals s. Substituting s for $[Ag^+]$ and $[I^-]$, the K_{sp} expression becomes

$$[Ag^+][I^-] = (s)(s) = s^2 = 8.5 \times 10^{-17}$$
$$s = \sqrt{8.5 \times 10^{-17}} = 9.2 \times 10^{-9} \text{ mol/L.}$$

The solubility of AgI is 9.2×10^{-9} mol/L at 298 K.

EXAMPLE PROBLEM 18-5

Calculating Molar Solubility from K_{sp}

Use the K_{sp} value from **Table 18-3** to calculate the solubility in mol/L of copper(II) carbonate ($CuCO_3$) at 298 K.

1. Analyze the Problem

You have been given the solubility product constant for $CuCO_3$. The copper and carbonate ion concentrations are in a one-to-one relationship with the molar solubility of $CuCO_3$. Use the solubility product constant expression to solve for the solubility. Because K_{sp} is of the order of 10^{-10}, you can predict that the solubility will be the square root of K_{sp}, or about 10^{-5}.

Known	Unknown
K_{sp} ($CuCO_3$) = 2.5×10^{-10}	solubility of $CuCO_3$ = ? mol/L

2. Solve for the Unknown

Write the balanced chemical equation for the solubility equilibrium and the solubility product constant expression.

$$CuCO_3(s) \rightleftharpoons Cu^{2+}(aq) + CO_3^{2-}(aq)$$

$$K_{sp} = [Cu^{2+}][CO_3^{2-}] = 2.5 \times 10^{-10}$$

Relate the solubility to $[Cu^{2+}]$ and $[CO_3^{2-}]$.

$$s = [Cu^{2+}] = [CO_3^{2-}]$$

Substitute s for $[Cu^{2+}]$ and $[CO_3^{2-}]$ and solve for s.

$$(s)(s) = s^2 = 2.5 \times 10^{-10}$$

$$s = \sqrt{2.5 \times 10^{-10}} = 1.6 \times 10^{-5} \text{ mol/L}$$

The molar solubility of $CuCO_3$ in water at 298 K is 1.6×10^{-5} mol/L.

3. Evaluate the Answer

The K_{sp} value has two significant figures, so the answer is correctly expressed with two digits. As predicted, the molar solubility of $CuCO_3$ is approximately 10^{-5} mol/L.

Finely ground copper carbonate is added to cattle and poultry feed to supply the necessary element, copper, to animal diets.

For more practice using the solubility product constant expression, go to **Supplemental Practice Problems** in Appendix A.

PRACTICE PROBLEMS

17. Use the data in **Table 18-3** to calculate the solubility in mol/L of these ionic compounds at 298 K.

a. $PbCrO_4$

b. AgCl

c. $CaCO_3$

d. $CaSO_4$

You have learned that the solubility product constant can be used to determine the molar solubility of an ionic compound. You can apply this information as you do the **CHEMLAB** at the end of this chapter. K_{sp} also can be used to find the concentrations of the ions in a saturated solution.

EXAMPLE PROBLEM 18-6

Calculating Ion Concentration from K_{sp}

Magnesium hydroxide is a white solid that is processed from seawater. Determine the hydroxide ion concentration at 298 K in a saturated solution of $Mg(OH)_2$ if the K_{sp} equals 5.6×10^{-12}.

1. Analyze the Problem

You have been given the K_{sp} for $Mg(OH)_2$. The moles of Mg^{2+} ions in solution equal the moles of $Mg(OH)_2$ that dissolved, but the moles of OH^- ions in solution are two times the moles of $Mg(OH)_2$ that dissolved. You can use these relationships to write the solubility product constant expression in terms of one unknown. Because the equilibrium expression is a third power equation, you can predict that $[OH^-]$ will be approximately the cube root of 10^{-12}, or approximately 10^{-4}.

Known	Unknown
$K_{sp} = 5.6 \times 10^{-12}$	$[OH^-] = ?$ mol/L

2. Solve for the Unknown

Write the equation for the solubility equilibrium and the K_{sp} expression.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 5.6 \times 10^{-12}$$

Let x equal $[Mg^{2+}]$. Because there are two OH^- ions for every Mg^{2+} ion, $[OH^-] = 2x$. Substitute these terms into the K_{sp} expression and solve for x.

$$(x)(2x)^2 = 5.6 \times 10^{-12}$$

$$(x)(4)(x)^2 = 5.6 \times 10^{-12}$$

$$4x^3 = 5.6 \times 10^{-12}$$

$$x^3 = \frac{5.6 \times 10^{-12}}{4} = 1.4 \times 10^{-12}$$

$$x = [Mg^{2+}] = \sqrt[3]{1.4 \times 10^{-12}} = 1.1 \times 10^{-4}\ \text{mol/L}$$

Multiply $[Mg^{2+}]$ by 2 to obtain $[OH^-]$.

$$[OH^-] = 2[Mg^{2+}] = 2(1.1 \times 10^{-4}\ \text{mol/L}) = 2.2 \times 10^{-4}\ \text{mol/L}$$

3. Evaluate the Answer

The given K_{sp} has two significant figures, so the answer is correctly stated with two digits. As predicted, $[OH^-]$ is about 10^{-4} mol/L.

This thick white suspension of magnesium hydroxide ($Mg(OH)_2$) is the antacid milk of magnesia. Because $Mg(OH)_2$ is only sparingly soluble, few formula units are in solution. These will be neutralized by stomach acid and then others will dissolve. Can you explain that statement using Le Châtelier's principle?

CONTENTS

PRACTICE PROBLEMS

18. Use K_{sp} values from **Table 18-3** to calculate the following.
- **a.** $[Ag^+]$ in a solution of AgBr at equilibrium
- **b.** $[F^-]$ in a saturated solution of CaF_2
- **c.** $[Ag^+]$ in a solution of Ag_2CrO_4 at equilibrium
- **d.** the solubility of PbI_2

For more practice using the solubility product constant expression, go to **Supplemental Practice Problems** in Appendix A.

Predicting precipitates You have seen that solubility product constants are useful for finding the solubility of an ionic compound and for calculating the concentrations of ions in a saturated solution. You also can use K_{sp} to predict whether a precipitate will form when two ionic solutions are mixed. For example, will a precipitate form when equal volumes of 0.10*M* aqueous solutions of iron(III) chloride ($FeCl_3$) and potassium hexacyanoferrate(II) ($K_4Fe(CN)_6$) are poured together? A double-replacement reaction might occur according to this equation.

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow 12KCl + Fe_4(Fe(CN)_6)_3$$

A precipitate is likely to form only if either product, KCl or $Fe_4(Fe(CN)_6)_3$, has low solubility. You are probably aware that KCl is a soluble compound and would be unlikely to precipitate. However, the K_{sp} for $Fe_4(Fe(CN)_6)_3$ is a very small number, 3.3×10^{-41}, which suggests that $Fe_4(Fe(CN)_6)_3$ might be expected to precipitate if the concentrations of its ions are large enough. Perhaps you are wondering how large is large enough.

The following equilibrium is possible between solid $Fe_4(Fe(CN)_6)_3$ (a precipitate) and its ions in solution, Fe^{3+} and $Fe(CN)_6^{4-}$.

$$Fe_4(Fe(CN)_6)_3(s) \rightleftharpoons 4Fe^{3+}(aq) + 3Fe(CN)_6^{4-}(aq)$$

When the two solutions are mixed, if the concentrations of the ions Fe^{3+} and $Fe(CN)_6^{4-}$ are greater than those that can exist in a saturated solution of $Fe_4(Fe(CN)_6)_3$, the equilibrium will shift to the left and $Fe_4(Fe(CN)_6)_3(s)$ will precipitate. To make a prediction, then, the ion concentrations must be calculated.

Table 18-4 shows the concentrations of the ions of reactants and products in the original solutions (0.10*M* $FeCl_3$ and 0.10*M* $K_4Fe(CN)_6$) and in the mixture immediately after equal volumes of the two solutions were mixed. Note that $[Cl^-]$ is three times as large as $[Fe^{3+}]$ because the ratio of Cl^- to Fe^{3+} in $FeCl_3$ is 3:1. Also note that $[K^+]$ is four times as large as $[Fe(CN)_6^{4-}]$ because the ratio of K^+ to $Fe(CN)_6^{4-}$ in $K_4Fe(CN)_6$ is 4:1. In addition, note that the concentration of each ion in the mixture is one-half its original concentration. This is because when equal volumes of two solutions are mixed, the same number of ions are dissolved in twice as much solution, so the concentration is reduced by one-half.

Table 18-4

Ion Concentrations in Original and Mixed Solutions

Original solutions (mol/L)	Mixture (mol/L)
$[Fe^{3+}] = 0.10$	$[Fe^{3+}] = 0.050$
$[Cl^-] = 0.30$	$[Cl^-] = 0.15$
$[K^+] = 0.40$	$[K^+] = 0.20$
$[Fe(CN)_6^{4-}] = 0.10$	$[Fe(CN)_6^{4-}] = 0.050$

You can now use the data in the table to make a trial to see if the concentrations of Fe^{3+} and $Fe(CN)_6^{4-}$ in the mixed solution exceed the value of K_{sp} when substituted into the solubility product constant expression.

$$K_{sp} = [Fe^{3+}]^4[Fe(CN)_6^{4-}]^3$$

But first, remember that you have not determined whether the solution is saturated. When you make this substitution, it will not necessarily give the solubility product constant. Instead, it provides a number called the ion product, Q_{sp}. Q_{sp} is a trial value that can be compared with K_{sp}.

$$Q_{sp} = [Fe^{3+}]^4[Fe(CN)_6^{\ 4-}]^3 = (0.050)^4(0.050)^3 = 7.8 \times 10^{-10}$$

You can now compare Q_{sp} and K_{sp}. This comparison can have one of three outcomes: Q_{sp} can be less than K_{sp}, equal to K_{sp}, or greater than K_{sp}.

1. If $Q_{sp} < K_{sp}$, the solution is unsaturated. No precipitate will form.
2. If $Q_{sp} = K_{sp}$, the solution is saturated and no change will occur.
3. If $Q_{sp} > K_{sp}$, a precipitate will form reducing the concentrations of the ions in the solution until the product of their concentrations in the K_{sp} expression equals the numerical value of K_{sp}. Then the system is in equilibrium and the solution is saturated.

In the case of the $Fe_4(Fe(CN)_6)_3$ equilibrium, Q_{sp} (7.8×10^{-10}) is larger than K_{sp} (3.3×10^{-41}) so a deeply colored blue precipitate of $Fe_4(Fe(CN)_6)_3$ forms, as you can see in **Figure 18-15.** Example Problem 18-7 and the **problem-solving LAB** on the following page will give you practice in calculating Q_{sp} to predict precipitates.

Figure 18-15

Because the ion product constant (Q_{sp}) is greater than K_{sp}, you could predict that this precipitate of $Fe_4(Fe(CN)_6)_3$ would form.

EXAMPLE PROBLEM 18-7

Predicting a Precipitate

Predict whether a precipitate of $PbCl_2$ will form if 100 mL of 0.0100*M* NaCl is added to 100 mL of 0.0200*M* $Pb(NO_3)_2$.

1. Analyze the Problem

You have been given equal volumes of two solutions with known concentrations. The concentrations of the initial solutions allow you to calculate the concentrations of Pb^{2+} and Cl^- ions in the mixed solution. The initial concentrations, when multiplied together in the solubility product constant expression, give an ion product of the order of 10^{-6}, so it is probable that after dilution, Q_{sp} will be less than K_{sp} (1.7×10^{-5}) and $PbCl_2$ will not precipitate.

Known	Unknown
100 mL 0.0100*M* NaCl	$Q_{sp} > K_{sp}$?
100 mL 0.0200*M* $Pb(NO_3)_2$	
$K_{sp} = 1.7 \times 10^{-5}$	

The peeling lead-based paint on this building is a hazard to small children who sometimes ingest small pieces of paint. Lead can build up in the body and cause many physical symptoms as well as brain damage and mental retardation.

2. Solve for the Unknown

Write the equation for the dissolving of $PbCl_2$ and the ion product expression, Q_{sp}.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$Q_{sp} = [Pb^{2+}][Cl^-]^2$$

Divide the concentrations of Cl^- and Pb^{2+} in half because on mixing, the volume doubles.

$$[Cl^-] = \frac{0.0100M}{2} = 0.00500M$$

$$[Pb^{2+}] = \frac{0.0200M}{2} = 0.0100M$$

Substitute these values into the ion product expression.

$$Q_{sp} = (0.0100)(0.00500)^2 = 2.5 \times 10^{-7}$$

Compare Q_{sp} with K_{sp}.

$$Q_{sp}\ (2.5 \times 10^{-7}) < K_{sp}\ (1.7 \times 10^{-5})$$

A precipitate will not form.

3. Evaluate the Answer

As predicted, Q_{sp} is less than K_{sp}. The Pb^{2+} and Cl^- ions are not present in high enough concentrations in the mixed solution to cause precipitation to occur.

PRACTICE PROBLEMS

19. Use K_{sp} values from **Table 18-3** to predict whether a precipitate will form when equal volumes of the following aqueous solutions are mixed.
a. 0.10*M* $Pb(NO_3)_2$ and 0.030*M* NaF
b. 0.25*M* K_2SO_4 and 0.010*M* $AgNO_3$
c. 0.20*M* $MgCl_2$ and 0.0025*M* NaOH

Practice!

For more practice predicting precipitates, go to **Supplemental Practice Problems** in Appendix A.

Common Ion Effect

The solubility of lead chromate ($PbCrO_4$) in water is 4.8×10^{-7} mol/L at 298 K. That means you can dissolve 4.8×10^{-7} mol $PbCrO_4$ in 1.00 L of pure water. However, you can't dissolve 4.8×10^{-7} mol $PbCrO_4$ in 1.00 L of 0.10*M* aqueous potassium chromate (K_2CrO_4) solution at that temperature. Why is $PbCrO_4$ less soluble in an aqueous K_2CrO_4 solution than in pure water?

problem-solving LAB

How does fluoride prevent tooth decay?

Using Numbers During the last half century, tooth decay has decreased significantly because minute quantities of fluoride ion ($6 \times 10^{-5}M$) are being added to most public drinking water and many people are using toothpastes containing sodium fluoride or tin(II) fluoride. Use what you know about the solubility of ionic compounds and reversible reactions to explore the role of the fluoride ion in maintaining cavity-free teeth.

Analysis

Tooth enamel, the hard, protective outer layer of the tooth, is 98% hydroxyapatite ($Ca_5(PO_4)_3OH$). Although quite insoluble ($K_{sp} = 6.8 \times 10^{-37}$ in water), demineralization, which is the dissolving of hydroxyapatite, does occur especially when the saliva contains acids. The reverse reaction, remineralization, also occurs. Remineralization is the re-depositing of tooth enamel. When hydroxyapatite is in solution with fluoride ions, a double-replacement reaction can occur. Fluoride ion replaces the hydroxide ion to form fluoroapatite ($Ca_5(PO_4)_3F$, $K_{sp} = 1 \times 10^{-60}$). Fluoroapatite remineralizes the tooth enamel, thus partially displacing hydroxyapatite. Because fluoroapatite is less soluble than hydroxyapatite, destructive demineralization is reduced.

Thinking Critically

1. Write the equation for the dissolving of hydroxyapatite and its equilibrium constant expression. How do the conditions in the mouth differ from those of a true equilibrium?
2. Write the equation for the double-replacement reaction that occurs between hydroxyapatite and sodium fluoride.
3. Calculate the solubility of hydroxyapatite and fluoroapatite in water. Compare the solubilities.
4. What is the ion product constant (Q_{sp}) for the reaction if 0.00050*M* NaF is mixed with an equal volume of 0.000015*M* $Ca_5(PO_4)_3OH$? Will a precipitate form (re-mineralization)?

Figure 18-16

In a solution of $PbCrO_4$ in pure water, $[Pb^{2+}]$ and $[CrO_4^{2-}]$ are equal. But in a solution with a common CrO_4^{2-} ion, $[Pb^{2+}]$ is much less than $[CrO_4^{2-}]$. In each case, however, the product of the two ions equals K_{sp} and the solubility of $PbCrO_4$ equals $[Pb^{2+}]$.

$$[Pb^{2+}][CrO_4^{2-}] = 2.3 \times 10^{-13} \text{ (in water)}$$

$$[Pb^{2+}]\Big[CrO_4^{2-}\Big] = 2.3 \times 10^{-13} \text{ (in } 0.10M\ K_2CrO_4)$$

The equation for the $PbCrO_4$ solubility equilibrium and the solubility product constant expression are

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq).$$

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.3 \times 10^{-13}$$

Recall that K_{sp} is a constant at any given temperature, so if the concentration of either Pb^{2+} or CrO_4^{2-} increases when the system is at equilibrium, the concentration of the other ion must decrease. The product of the concentrations of the two ions must always equal K_{sp}. The K_2CrO_4 solution contains CrO_4^{2-} ions before any $PbCrO_4$ dissolves. In this example, the CrO_4^{2-} ion is called a common ion because it is part of both $PbCrO_4$ and K_2CrO_4. A **common ion** is an ion that is common to two or more ionic compounds. The lowering of the solubility of a substance by the presence of a common ion is called the **common ion effect.**

Figure 18-16 illustrates how the balance between the ion concentrations differs in a solution of $PbCrO_4$ in pure water and in a 0.10*M* solution of K_2CrO_4. In each case, $[Pb^{2+}]$ represents the solubility of $PbCrO_4$.

The common ion effect and Le Châtelier's principle A saturated solution of lead chromate ($PbCrO_4$) is shown in **Figure 18-17a.** Note the solid yellow $PbCrO_4$ in the bottom of the test tube. The solution and solid are in equilibrium according to this equation.

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

When a solution of $Pb(NO_3)$ is added to the saturated $PbCrO_4$ solution, more solid $PbCrO_4$ precipitates, as you can see in **Figure 18-17b.** The Pb^{2+} ion, common to both $Pb(NO_3)_2$ and $PbCrO_4$, reduces the solubility of $PbCrO_4$. Can this precipitation of $PbCrO_4$ be explained by Le Châtelier's principle? Adding Pb^{2+} ion to the solubility equilibrium stresses the equilibrium. To relieve the stress, the equilibrium shifts to the left to form more solid $PbCrO_4$.

The common ion effect also plays a role in the use of barium sulfate ($BaSO_4$) when X rays are taken of the digestive system. Recall that patients who need such X rays must drink a mixture containing $BaSO_4$. The low solubility of $BaSO_4$ helps ensure that the amount of the toxic barium ion absorbed into patient's system is small enough to be harmless. The procedure is further safe-guarded by the addition of sodium sulfate (Na_2SO_4), a soluble ionic compound that provides a common ion, SO_4^{2-}. How does the additional SO_4^{2-} affect the concentration of barium ion in the mixture that patients must drink?

Figure 18-17

In **a**, $PbCrO_4(s)$ is in equilibrium with its ions in solution. Then, in **b**, the equilibrium is stressed by the addition of $Pb(NO_3)_2$ and more $PbCrO_4$ precipitate forms. Use the equation and Le Châtelier's principle to convince yourself that a shift to the left occurred. Then write the K_{sp} for this reaction as in **Figure 18-16.**

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Le Châtelier's principle predicts that additional SO_4^{2-} from the Na_2SO_4 will shift the equilibrium to the left to produce more solid $BaSO_4$ and reduce the number of harmful Ba^{2+} ions in solution.

Solubility Equilibria in the Laboratory

Suppose you are given a clear aqueous solution and told that it could contain almost any of the ions formed by the common metallic elements. Your job is to find out which ions the solution contains. It seems an impossible task, but chemists have worked out a scheme that allows you to separate and identify many common metal ions. The scheme is based upon the differing solubilities of the ions. For example, only three ions form insoluble chlorides—Ag^+, Pb^{2+}, and Hg_2^{2+}. That may give you an idea of how you could proceed. If you add HCl to your solution, those three ions will precipitate as a white solid that would contain AgCl(s), $PbCl_2$(s), and Hg_2Cl_2(s) if all three of the metal ions are present. The ions that do not form insoluble chlorides will be left in the clear solution, which can be separated from the white solid.

Is $PbCl_2$ present in the white solid? To find out, you can use the fact that $PbCl_2$ is soluble in hot water but AgCl and Hg_2Cl_2 are not. After adding water and heating the mixture of chlorides, you can separate the liquid (that could contain dissolved $PbCl_2$) from AgCl and Hg_2Cl_2, which are still in solid form. What test could you use to show that the separated liquid contains Pb^{2+}? Remember that $PbCrO_4$ is a sparingly soluble compound. You could add K_2CrO_4. If a yellow precipitate of $PbCrO_4$ forms, you have proof of the presence of Pb^{2+}.

Are Hg_2Cl_2, or AgCl, or both compounds present in the remaining precipitate? Silver chloride is soluble in ammonia; mercury(I) chloride forms a black precipitate with ammonia. Suppose you add ammonia and get a black precipitate. You can conclude that Hg_2^{2+} is present. But did AgCl dissolve in ammonia, or was all the white precipitate Hg_2Cl_2? To find out, you can add HCl to the solution. HCl will interact with the ammonia in the solution and cause AgCl to precipitate again.

The procedure you have been reading is just one step in the complete analysis of the initial solution of ions. **Figure 18-18** is a flow chart of the steps in the procedure. Follow the chart step by step through each identification. Note that as each reactant is added (HCl, hot water, NH_3), a separation is made between those ions that are soluble and those that are not.

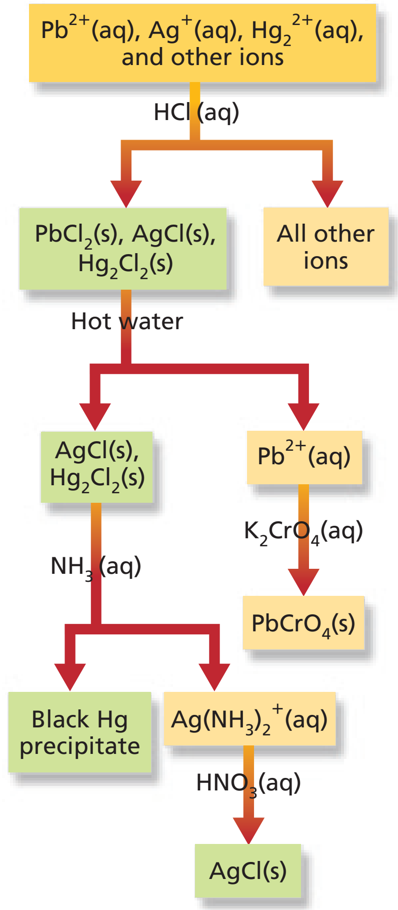


Figure 18-18

Follow the process down the chart. The reactants added at each step are written on the downward arrows. Which reactions are separations? Which reactions confirm the presence of an ion?

Section 18.3 Assessment

20. List the information you would need in order to calculate the concentration of a product in a reaction mixture at equilibrium.

21. How can you use the solubility product constant to calculate the solubility of a sparingly soluble ionic compound?

22. What is a common ion? Explain how a common ion reduces the solubility of an ionic compound.

23. Thinking Critically When aqueous solutions of two ionic compounds are mixed, how does Q_{sp} relate to K_{sp} for a possible precipitate?

24. Designing an Experiment An aqueous solution is known to contain either Mg^{2+} or Pb^{2+}. Design an experiment based on solubilities that would help you determine which of the two ions is present. The solubilities of many ionic compounds are given in **Table C-10** in Appendix C.

Comparing Two Solubility Product Constants

Le Châtelier's principle is a powerful tool for explaining how a reaction at equilibrium shifts when a stress is placed on the system. In this experiment, you can use Le Châtelier's principle to evaluate the relative solubilities of two precipitates. By observing the formation of two precipitates in the same system, you can infer the relationship between the solubilities of the two ionic compounds and the numerical values of their solubility product constants (K_{sp}). You will be able to verify your own experimental results by calculating the molar solubilities of the two compounds using the K_{sp} for each compound.

Problem

How can a saturated solution of one ionic compound react with another ionic compound to form another precipitate? What is the relationship between solubility and the K_{sp} value of a saturated solution?

Objectives

- **Observe** evidence that a precipitate is in equilibrium with its ions in solution.
- **Infer** the relative solubilities of two sparingly soluble ionic compounds.
- **Compare** the values of the K_{sp} for two different compounds and relate them to your observations.
- **Explain** your observations of the two precipitates by using Le Châtelier's principle.
- **Calculate** the molar solubilities of the two ionic compounds from their K_{sp} values.

Materials

$AgNO_3$ solution
NaCl solution
Na_2S solution
24-well microplate
thin-stem pipettes (3)
wash bottle

Safety Precautions

- **Always wear safety goggles, gloves, and a lab apron.**
- **Silver nitrate is highly toxic and will stain skin and clothing.**

Pre-Lab

1. Read the entire **CHEMLAB**.
2. Prepare all written materials that you will take into the laboratory. Be sure to include safety precautions, procedure notes, and a data table in which to record your observations.
3. State Le Châtelier's principle.
4. Identify the control and the independent variable in the experiment.
5. When a solid dissolves to form two ions and the solid's K_{sp} is known, what is the mathematical formula you can use to calculate the molar solubility?

Precipitate Formation

	Observations
Step 3	
Step 5	
Step 6	

Procedure

1. Place 10 drops of $AgNO_3$ solution in well A1 of a 24-well microplate. Place 10 drops of the same solution in well A2.
2. Add 10 drops of NaCl solution to well A1 and 10 drops to well A2.

3. Allow the precipitate to form in each well. Record your observations.
4. To well A2, add 10 drops of Na_2S solution.
5. Allow the precipitate to form. Record your observations of the precipitate.
6. Compare the contents of wells A1 and A2 and record your observations in your table.

Cleanup and Disposal

1. Use a wash bottle to transfer the contents of the well plate into a large waste beaker.
2. Wash your hands thoroughly after all lab work and cleanup are complete.

Analyze and Conclude

1. **Analyzing Information** Write the complete equation for the double-replacement reaction that occurred when NaCl and $AgNO_3$ were mixed in wells Al and A2 in step 2. Write the net ionic equation.
2. **Analyzing Information** Write the solubility product constant expression for the equilibrium established in wells A1 and A2 in step 2. K_{sp} (AgCl) = 1.8×10^{-10}.
3. **Analyzing Information** Write the equation for the equilibrium that was established in well A2 when you added Na_2S. K_{sp} (Ag_2S) = 8×10^{-48}
4. **Inferring** Identify the two precipitates by color.
5. **Comparing and Contrasting** Compare the K_{sp} values for the two precipitates. Infer which of the two ionic compounds is more soluble.
6. **Recognizing Cause and Effect** Use Le Châtelier's principle to explain how the addition of Na_2S in procedure step 4 affected the equilibrium established in well A2.
7. **Using Numbers** Calculate the molar solubilities of the two precipitates using the K_{sp} values. Which of the precipitates is more soluble?
8. **Thinking Critically** What evidence from this experiment supports your answer to question 7? Explain.
9. **Error Analysis** Did you observe the well plate from the side as well as from the top? What did you notice?
10. **Developing General Rules** The solubility of an ionic compound depends upon the nature of the cations and anions that make up the compound. The reactants you used in this **CHEMLAB** are all soluble ionic compounds, whereas, the precipitates are insoluble. How does soluble Na_2S differ from insoluble Ag_2S? How does soluble NaCl differ from insoluble AgCl? Use this information and K_{sp} data from **Table 18-3** and the *Handbook of Chemistry and Physics* to develop general rules for solubility. What group of metal ions is not found in sparingly soluble compounds? What polyatomic ions, positive and negative, form only soluble ionic compounds? How does K_{sp} relate to a compound's relative solubility?

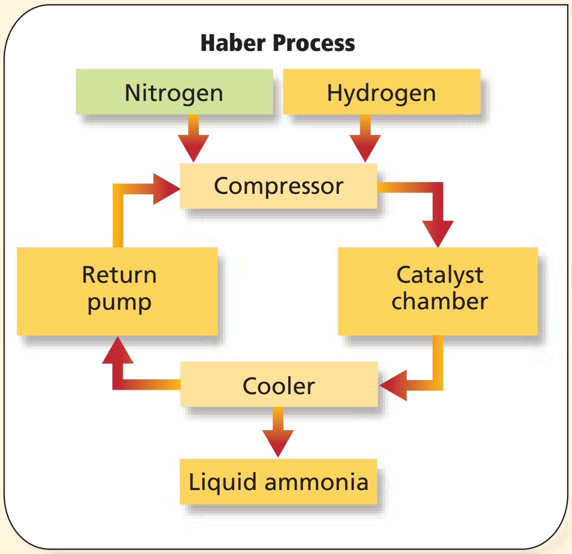
Real-World Chemistry

1. Research how industries use precipitation to remove hazardous chemicals from wastewater before returning it to the water cycle.
2. *Hard water* is the name given to water supplies that contain significant concentrations of Mg^{2+} and Ca^{2+} ions. Check on the solubility of ionic compounds formed with these ions and predict what problems they may cause.
3. Explain what would happen if you lost the stopper for a bottle of a saturated solution of lead sulfate ($PbSO_4$) and the bottle stood open to the air for a week. Would your answer be different if it were an unsaturated solution? Explain.

CHEMISTRY and Technology

The Haber Process

Diatomic nitrogen makes up about 79 percent of Earth's atmosphere. A few species of soil bacteria can use atmospheric nitrogen to produce ammonia (NH_3). Other species of bacteria then convert the ammonia into nitrite and nitrate ions, which can be absorbed and used by plants. Ammonia also can be synthesized.



Applying Le Châtelier's Principle

The process of synthesizing large amounts of ammonia from nitrogen and hydrogen gases was first demonstrated in 1909 by Fritz Haber, a German research chemist, and his English research assistant, Robert LeRossignol. The Haber process involves this reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$$

The process produces high yields of ammonia by manipulating three factors that influence the reaction—pressure, temperature, and catalytic action.

During the synthesis of ammonia, four molecules of reactant produce two molecules of product. According to Le Châtelier's principle, if the pressure on this reaction is increased, the forward reaction will speed up to reduce the stress because two molecules exert less pressure than four molecules. Increased pressure will also cause the reactants to collide more frequently, thus increasing the reaction rate. Haber's apparatus used a pressure of 2×10^5 kPa.

The forward reaction is favored by a low temperature because the stress caused by the heat generated by the reaction is reduced. But low temperature decreases the number of collisions between reactants, thus decreasing the rate of reaction. Haber compromised by using an intermediate temperature of about 450°C.

A catalyst is used to decrease the activation energy and thus, increase the rate at which equilibrium is reached. Haber used iron as a catalyst in his process.

The Industrial Process

Haber's process incorporated several operations that increased the yield of ammonia. The reactant gases entering the chamber were warmed by heat produced by the reaction. The reactant-product mixture was allowed to cool slowly after reacting over the catalyst. Ammonia gas was removed from the process by liquefication, and the unreacted nitrogen and hydrogen were recycled back into the process.

Carl Bosch, a German industrial chemist improved Haber's process by designing new reaction chambers, improving pressurizing pumps, and finding inexpensive catalysts. By 1913, Bosch had built the first plant for synthesizing ammonia in Oppau, Germany.

Investigating the Technology

1. **Thinking Critically** How does removing ammonia from the process affect equilibrium?
2. **Using Resources** Research how ammonia is used in the production of many agricultural fertilizers and other products.

CHEMISTRY Online

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Visit the Chemistry Web site at **science.glencoe.com** to find links to more information about the Haber process and ammonia.

Summary

18.1 Equilibrium: A State of Dynamic Balance

- A reversible reaction is one that can take place in both the forward and reverse directions.
- A reversible reaction leads to an equilibrium state in which the forward and reverse reactions take place at equal rates and the concentrations of reactants and products remain constant.
- You can write the equilibrium constant expression for an equilibrium system using the law of chemical equilibrium.
- The equilibrium constant expression is a ratio of the molar concentrations of the products divided by the molar concentrations of the reactants with all concentrations in the ratio raised to a power equal to their coefficients in the balanced chemical equation.
- The value of the equilibrium constant expression, K_{eq}, is a constant for a given temperature.
- A large value for K_{eq} means that the products are favored at equilibrium; a small K_{eq} value means that the reactants are favored.
- You can calculate K_{eq} by substituting known equilibrium concentrations into the equilibrium constant expression.

18.2 Factors Affecting Chemical Equilibrium

- Le Châtelier's principle describes how an equilibrium system shifts in response to a stress or disturbance. A stress is any change in the system at equilibrium.
- An equilibrium can be forced in the direction of the products by adding a reactant or by removing a product. It can be forced in the direction of the reactants by adding a product or removing a reactant.
- When an equilibrium shifts in response to a change in concentration or volume, the equilibrium position changes but K_{eq} remains constant. A change in temperature, however, alters both the equilibrium position and the value of K_{eq}.

18.3 Using Equilibrium Constants

- Given K_{eq}, the equilibrium concentration of a substance can be calculated if you know the equilibrium concentrations of all other reactants and products.
- The solubility product constant expression, K_{sp}, describes the equilibrium between a sparingly soluble ionic compound and its ions in solution.
- You can calculate the molar solubility of an ionic compound using the solubility product constant expression.
- The ion product, Q_{sp}, can be calculated from the molar concentrations of the ions in a solution and compared with the K_{sp} to determine whether a precipitate will form when two solutions are mixed.
- The solubility of a substance is lower when the substance is dissolved in a solution containing a common ion. This is called the common ion effect.

Key Equations and Relationships

- $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ (p. 563)

Vocabulary

- chemical equilibrium (p. 561)
- common ion (p. 584)
- common ion effect (p. 584)
- equilibrium constant (p. 563)
- heterogeneous equilibrium (p. 565)
- homogeneous equilibrium (p. 564)
- law of chemical equilibrium (p. 563)
- Le Châtelier's principle (p. 569)
- reversible reaction (p. 560)
- solubility product constant (p. 578)

CHAPTER 18 ASSESSMENT

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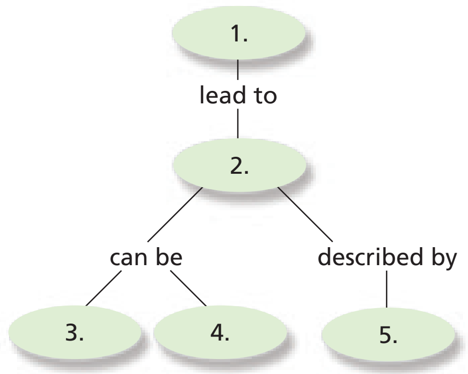
Go to the Chemistry Web site at **science.glencoe.com** *or use the* **Chemistry CD-ROM** *for additional Chapter 18 Assessment.*

Concept Mapping

25. Fill in the spaces on the concept map with the following phrases: equilibrium constant expressions, reversible reactions, heterogeneous equilibria, homogeneous equilibria, chemical equilibria.



Mastering Concepts

26. Describe an equilibrium in everyday life that illustrates a state of balance between two opposing processes. (18.1)

27. Given the fact that the concentrations of reactants and products are not changing, why is the word *dynamic* used for describing chemical equilibrium? (18.1)

28. How can you indicate in a chemical equation that a reaction is reversible? (18.1)

29. Although the general equation for a chemical reaction is reactants → products, explain why this equation is not complete for a system at equilibrium. (18.1)

30. Explain the difference between a homogeneous equilibrium and a heterogeneous equilibrium. (18.1)

31. What is an equilibrium position? (18.1)

32. Explain how to use the law of chemical equilibrium in writing an equilibrium constant expression. (18.1)

33. Why does a numerically large K_{eq} mean that the products are favored in an equilibrium system? (18.1)

34. Why should you pay attention to the physical states of all reactants and products when writing equilibrium constant expressions? (18.1)

35. How can an equilibrium system contain small and unchanging amounts of products yet have large amounts of reactants? What can you say about the relative size of K_{eq} for such an equilibrium? (18.1)

36. Describe the opposing processes in the physical equilibrium that exists in a closed container half-filled with liquid ethanol. (18.1)

37. What is meant by a stress on a reaction at equilibrium? (18.2)

38. How does Le Châtelier's principle describe an equilibrium's response to a stress? (18.2)

39. Why does removing a product cause an equilibrium to shift in the direction of the products? (18.2)

40. When an equilibrium shifts toward the reactants in response to a stress, how is the equilibrium position changed? (18.2)

41. Use Le Châtelier's principle to explain how a shift in the equilibrium $H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$ causes a soft drink to go flat when its container is left open to the atmosphere. (18.2)

42. How is K_{eq} changed when heat is added to an equilibrium in which the forward reaction is exothermic? Explain using Le Châtelier's principle. (18.2)

43. Changing the volume of the system alters the equilibrium position of this equilibrium.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

But a similar change has no effect on this equilibrium.

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

Explain. (18.2)

44. How might the addition of a noble gas to the reaction vessel affect this equilibrium?

$2N_2H_4(g) + 2NO_2(g) \rightleftharpoons 3N_2(g) + 4H_2O(g)$

Assume that the volume of the reaction vessel does not change. (18.2)

45. When an equilibrium shifts to the right, what happens to the following? (18.2)

a. the concentrations of the reactants
b. the concentrations of the products

46. How would each of the following changes affect the equilibrium position of the system used to produce methanol from carbon monoxide and hydrogen? (18.2)

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$

a. adding CO to the system
b. cooling the system
c. adding a catalyst to the system
d. removing CH_3OH from the system
e. decreasing the volume of the system

47. Why is the concentration of a solid not included as part of the solubility product constant? (18.3)

48. What does it mean to say that two solutions have a common ion? Give an example that supports your answer. (18.3)

49. Explain the difference between Q_{sp} and K_{sp}. (18.3)

50. Explain why a common ion lowers the solubility of an ionic compound. (18.3)

51. Describe the solution that results when two solutions are mixed and Q_{sp} is found to equal K_{sp}. Does a precipitate form?

Mastering Problems

The Equilibrium Constant Expression (18.1)

52. Write equilibrium constant expressions for these homogeneous equilibria.

a. $2N_2H_4(g) + 2NO_2(g) \rightleftharpoons 3N_2(g) + 4H_2O(g)$
b. $2NbCl_4(g) \rightleftharpoons NbCl_3(g) + NbCl_5(g)$
c. $I_2(g) \rightleftharpoons 2I(g)$
d. $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

53. Write equilibrium constant expressions for these heterogeneous equilibria.

a. $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$
b. $C_6H_6(l) \rightleftharpoons C_6H_6(g)$
c. $Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)$

54. Pure water has a density of 1.00 g/mL at 297 K. Calculate the molar concentration of pure water at this temperature.

55. Calculate K_{eq} for the following equilibrium when $[SO_3] = 0.0160$ mol/L, $[SO_2] = 0.00560$ mol/L, and $[O_2] = 0.00210$ mol/L.

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

56. K_{eq} for this reaction is 3.63.

$A + 2B \rightleftharpoons C$

The data in the table shows the concentrations of the reactants and product in two different reaction mixtures at the same temperature. Does the data provide evidence that both reactions are at equilibrium?

Table 18-5

Concentrations of A, B, and C		
A (mol/L)	**B (mol/L)**	**C (mol/L)**
0.500	0.621	0.700
0.250	0.525	0.250

57. When solid ammonium chloride is put in a reaction vessel at 323 K, the equilibrium concentrations of both ammonia and hydrogen chloride are found to be 0.0660 mol/L. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$. Calculate K_{eq}.

58. Suppose you have a cube of pure manganese metal measuring 5.25 cm on each side. You find that the mass of the cube is 1076.6 g. What is the molar concentration of manganese in the cube?

Le Châtelier's Principle (18.2)

59. Use Le Châtelier's principle to predict how each of the following changes would affect this equilibrium.
$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

a. adding $H_2O(g)$ to the system
b. removing $CO(g)$ from the system
c. adding $H_2(g)$ to the system
d. adding something to the system to absorb $CO_2(g)$

60. How would increasing the volume of the reaction vessel affect these equilibria?

a. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

61. How would decreasing the volume of the reaction vessel affect these equilibria?

a. $2N_2H_4(g) + 2NO_2(g) \rightleftharpoons 3N_2(g) + 4H_2O(g)$
b. $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

62. How would these equilibria be affected by increasing the temperature?

a. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + \text{heat}$
b. $\text{heat} + NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$

63. Ethylene (C_2H_4) reacts with hydrogen to form ethane (C_2H_6).
$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) + \text{heat}$
How would you regulate the temperature of this equilibrium in order to do the following?

a. increase the yield of ethane
b. decrease the concentration of ethylene
c. increase the amount of hydrogen in the system

64. How would simultaneously decreasing the temperature and volume of the system affect these equilibria?

a. $\text{heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
b. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + \text{heat}$

Calculations Using K_{eq} (18.3)

65. K_{eq} is 1.60 at 933 K for this reaction.
$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Calculate the equilibrium concentration of hydrogen when $[CO_2] = 0.320$ mol/L, $[H_2O] = 0.240$ mol/L, and $[CO] = 0.280$ mol/L.

66. At 2273 K, $K_{eq} = 6.2 \times 10^{-4}$ for the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

If $[N_2] = 0.05200$ mol/L and $[O_2] = 0.00120$ mol/L, what is the concentration of NO at equilibrium?

Calculations Using K_{sp} (18.3)

67. Calculate the ion product to determine if a precipitate will form when 125 mL 0.00500*M* sodium chloride is mixed with 125 mL 0.00100*M* silver nitrate solution.

68. Calculate the molar solubility of strontium chromate in water at 298 K if $K_{sp} = 3.5 \times 10^{-5}$.

69. Will a precipitate form when 1.00 L of 0.150*M* iron(II) chloride solution is mixed with 2.00 L of 0.0333*M* sodium hydroxide solution? Explain your reasoning and show your calculations.

Mixed Review

Sharpen your problem-solving skills by answering the following.

70. How many moles per liter of silver chloride will be in a saturated solution of AgCl? $K_{sp} = 1.8 \times 10^{-10}$

71. A 6.00-L vessel contains an equilibrium mixture of 0.0222 mol PCl_3, 0.0189 mol PCl_5, and 0.1044 mol Cl_2. Calculate K_{eq} for the following reaction.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

72. How would simultaneously increasing the temperature and volume of the system affect these equilibria?

a. $2O_3(g) \rightleftharpoons 3O_2(g)$ + heat
b. heat + $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

73. The solubility product constant for lead(II) arsenate ($Pb_3(AsO_4)_2$), is 4.0×10^{-36} at 298 K. Calculate the molar solubility of the compound at this temperature.

74. How would these equilibria be affected by decreasing the temperature?

a. $2O_3(g) \rightleftharpoons 3O_2(g)$ + heat
b. heat + $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

Thinking Critically

75. Predicting Suppose you're thinking about using the following reaction to produce hydrogen from hydrogen sulfide.

$2H_2S(g)$ + heat $\rightleftharpoons 2H_2(g) + S_2(g)$

Given that K_{eq} for the equilibrium is 2.27×10^{-4}, would you expect a high yield of hydrogen? Explain how you could regulate the volume of the reaction vessel and the temperature to increase the yield.

76. Applying Concepts Smelling salts, sometimes used to revive a groggy or unconscious person, are made of ammonium carbonate. The equation for the endothermic decomposition of ammonium carbonate is

$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$

Would you expect smelling salts to work as well on a cold winter day as on a warm summer day? Explain your answer.

77. Comparing and Contrasting Which of the two solids, calcium phosphate or iron(III) phosphate, has the greater molar solubility? K_{sp} $(Ca_3(PO_4)_2) = 1.2 \times 10^{-29}$; K_{sp} $(FePO_4) = 1.0 \times 10^{-22}$. Which compound has the greater solubility expressed in grams per liter?

78. Recognizing Cause and Effect You have 12.56 g of a mixture made up of sodium chloride and barium chloride. Explain how you could use a precipitation reaction to determine how much of each compound the mixture contains.

Writing in Chemistry

79. Research the role that solubility plays in the formation of kidney stones. Find out what compounds are found in kidney stones and their K_{sp} values. Summarize your findings in a report.

80. The presence of magnesium and calcium ions in water makes the water "hard." Explain in terms of solubility why the presence of these ions is often undesirable. Find out what measures can be taken to eliminate them.

Cumulative Review

Refresh your understanding of previous chapters by answering the following.

81. How are elctrons shared differently in H_2, O_2, and N_2? (Chapter 9)

82. How can you tell if a chemical equation is balanced? (Chapter 10)

83. What mass of carbon must burn to produce 4.56 L CO_2 gas at STP? (Chapter 14)

$C(s) + O_2(g) \rightarrow CO_2(g)$

84. When you reverse a thermochemical equation, why must you change the sign of ΔH? (Chapter 16)

Use these questions and the test-taking tip to prepare for your standardized test.

1. A system reaches chemical equilibrium when _____ .

a. no new product is formed by the forward reaction
b. the reverse reaction no longer occurs in the system
c. the concentration of reactants in the system is equal to the concentration of products
d. the rate at which the forward reaction occurs equals the rate of the reverse reaction

2. A value of K_{eq} greater than 1 means that _____ .

a. more reactants than products exist at equilibrium
b. more products than reactants exist at equilibrium
c. the rate of the forward reaction is high at equilibrium
d. the rate of the reverse reaction is high at equilibrium

3. The hydrogen sulfide produced as a byproduct of petroleum refinement can be used to produce elemental sulfur: $2H_2S(g) + SO_2(g) \rightarrow 3S(l) + 2H_2O(g)$

The equilibrium constant expression for this reaction is _____ .

a. $K_{eq} = \frac{[H_2O]}{[H_2S][SO_2]}$
b. $K_{eq} = \frac{[H_2S]^2[SO_2]}{[H_2S]^2}$
c. $K_{eq} = \frac{[H_2O]^2}{[H_2S]^2[SO_2]}$
d. $K_{eq} = \frac{[S]^3[H_2O]^2}{[H_2S]^2[SO_2]}$

4. The following system is in equilibrium:

$2S(s) + 5F_2(g) \rightleftharpoons SF_4(g) + SF_6(g)$

The equilibrium will shift to the right if _____ .

a. the concentration of SF_4 is increased
b. the concentration of SF_6 is increased
c. the pressure on the system is increased
d. the pressure on the system is decreased

Interpreting Tables Use the table to answer questions 5–7.

Concentration Data for the Equilibrium System $MnCO_3(s) \rightleftharpoons Mn^{2+}(aq) + CO_3^{2-}(aq)$ at 298 K

Trial	$[Mn^{2+}]_0$ (M)	$[CO_3^{2-}]_0$ (M)	$[Mn^{2+}]_{eq}$ (M)	$[CO_3^{2-}]_{eq}$ (M)
1	0.0000	0.00400	5.60×10^{-9}	4.00×10^{-3}
2	0.0100	0.0000	1.00×10^{-2}	2.24×10^{-9}
3	0.0000	0.0200	1.12×10^{-9}	2.00×10^{-2}

5. The K_{sp} for $MnCO_3$ is _____ .

a. 2.24×10^{-11}
b. 4.00×10^{-11}
c. 1.12×10^{-9}
d. 5.60×10^{-9}

6. What is the molar solubility of $MnCO_3$ at 298 K?

a. $4.73 \times 10^{-6}M$
b. $6.32 \times 10^{-2}M$
c. $7.48 \times 10^{-5}M$
d. $3.35 \times 10^{-5}M$

7. A 50.0-mL volume of $3.00 \times 10^{-6}M$ K_2CO_3 is mixed with 50.0 mL of $MnCl_2$. A precipitate of $MnCO_3$ will form only when the concentration of the $MnCl_2$ solution is greater than _____ .

a. $7.47 \times 10^{-6}M$
b. $1.49 \times 10^{-5}M$
c. $2.99 \times 10^{-5}M$
d. $1.02 \times 10^{-5}M$

8. Which of the following statements about the common ion effect is NOT true?

a. The effects of common ions on an equilibrium system can be explained by Le Châtelier's principle.
b. The decreased solubility of an ionic compound due to the presence of a common ion is called the common ion effect.
c. The addition of NaCl to a saturated solution of AgCl will produce the common ion effect.
d. The common ion effect is due to a shift in equilibrium towards the aqueous products of a system.

9. If the forward reaction of a system in equilibrium is endothermic, increasing the temperature of the system will _____ .

a. shift the equilibrium to the left
b. shift the equilibrium to the right
c. decrease the rate of the forward reaction
d. increase the rate of the reverse reaction

10. $Cl_2(g) + 3O_2(g) + F_2(g) \rightleftharpoons 2ClO_3F(g)$

The formation of perchloryl fluoride (ClO_3F) from its elements has an equilibrium constant of 3.42×10^{-9} at 298 K. If $[Cl_2] = 0.563M$, $[O_2] = 1.01M$, and $[ClO_3F] = 1.47 \times 10^{-5}M$ at equilibrium, what is the concentration of F_2?

a. $9.18 \times 10^{0}M$
b. $3.73 \times 10^{-10}M$
c. $1.09 \times 10^{-1}M$
d. $6.32 \times 10^{-2}M$

THE PRINCETON REVIEW **TEST-TAKING TIP**

Maximize Your Score If possible, find out how your standardized test will be scored. In order to do your best, you need to know if there is a penalty for guessing, and if so, what the penalty is. If there is no random-guessing penalty at all, you should always fill in an answer, even if you haven't read the question!